Solvent Selectivity of Liquid Ammonia for Pure Hydrocarbons

Tie-Line Data and Comparison of Selectivity with Other Solvents

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Introduction

Results of extensive studies on the separation of petroleum fractions with liquid ammonia as a solvent, which include the fundamental solubility relationships for various hydrocarbon types and the tests on pilot plant extractions, have recently been published and the utility and the versatility of liquid ammonia as a solvent were stressed[1]. The fact that liquid ammonia has good solvency and selectivity for separating mixtures of naphthenic and aromatic hydrocarbons was clarified through the studies on the system of methylcyclohexane—toluene—liquid ammonia. It has also been demonstrated that it is important to control the dissolving power of the ammonia solvent so that the amount of hydrocarbon in the solvent phase lies between about 10 and 30 weight % either by temperature reduction or water injection or both, in order to prevent the decrease of selectivity accompanied by the increase of solubility. However, from the viewpoint of phase equilibrium, apart what has just been stated above and the relative distribution ratio at 10% solubility, few fundamental equilibrium data are given.

In order to determine the solvency and selectivity of liquid ammonia as a solvent for separating more soluble hydrocarbons such as aromatics and low molecular weight hydrocarbons, systems of cyclohexane—benzene, *n*-hexane—benzene, and ethylbenzene—styrene, the last as an example of two aromatic hydrocarbons, whose separation is a practical problem, were selected, and equilibria of ternary systems of these two components and liquid ammonia were measured. Furthermore, the comparison of selectivity of liquid ammonia with other solvents, which are used or are usable for the separation of various hydrocarbons, was attempted.

Experimental Procedure and Materials

The equilibrium data were determined in the same way as described in Part I of this series[2,3]; *n*-hexane and cyclohexane used in the present study are the same materials as described in Part II[3].

Commercial benzene was purified by the usual method and the fraction of b.p. 80.0-80.1°C, m.p. 5.53°C, d_4^{20} 0.8784, n_D^{20} 1.5011, was used.

Ethylbenzene was prepared from bromobenzene and ethyl bromide by the Fittig reaction and was fractionated to obtain one, having constants of b.p. 136.0°C, d_4^{20} 0.8670, n_D^{20} 1.4959.

Styrene was kindly supplied by Nippon Paint Co., Ltd. (purchased from Dow Chemical Co.), and showed b.p.$_{24\cdot1}$ 48°C, d_4^{20} 0.9059, n_D^{20} 1.5468, and bromine number[4] of 151.2 (theoretical: 153.3).

The ternary system including styrene was prepared by the use of styrene freshly fractionated under reduced pressure, and after the determination of ammonia, the composition of the binary system of ethylbenzene and styrene was determined by measuring specific gravity, refractive index, and bromine number of the raffinate or the extract. For this system, no correction was made for the slight loss of hydrocarbons due to the volatilization during the determination of ammonia, because their vapor pressures at experimental temperatures are small and nearly of the same order.

Results

Equilibrium data for the system *n*-hexan-benzene-liquid ammonia (20°C) are shown in Table I, those for cyclohexane-benzene-liquid ammonia (20°C and 0°C) in Table II, and those for ethylbenzene-styrene-liquid ammonia (0°C and −15.5°C) in Table III. The data are presented graphically in Fig. 1–3. Both cyclohexane and benzene are present as crystals at 0°C, but their mixtures with liquid ammonia are liquids at 0°C lowering the melting point.

As will be clear from Fig. 1 and 2, aromatic hydrocarbons are selectively extracted from C_6-hydrocarbon mixtures,

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[1] M. R. Fenske, R. H. McCormick, H. Lawroski and R. G. Geier, *A. I. Ch. E. Journal*, **1**, 335 (1955).

[2] K. Ishida, *J. Chem. Soc. Japan*, *Ind. Chem. Sect.*, **56**, 469 (1953).

[3] Ibid , **57**, 479 (1954).

[4] H. L. Johnson and R. A. Clark, *Anal. Chem.*, **19**, 869 (1947).

showing little difference between the paraffinic and naphthenic hydrocarbon present as a diluent. This is in accordance with the expectation from the equilibrium data for the system *n*-hexane-cyclohexane-liquid ammonia[3].

It seems that the separation of aromatic hydrocarbon mixture with the same number of carbon atoms, which contains another compound having more highly unsaturated properties, will be possible by the extraction using liquid ammonia as a solvent, since the increase of unsaturated properties increases the solubility for the solvent. Table III and Fig. 3 indicate that liquid ammonia is also usable for such separation, and that when the extraction is carried out at –15.5°C, the mixture of ethylbenzene and styrene can be separated into the raffinate containing 5 wt. % styrene and the extract containing 98 wt. % styrene under the condition of total reflux with minimum number of theoretical stages of 15.

The composition at plait point in Tables I–III (b) was estimated from Hand plot[5] according to Treybal, et al[6]. The slope of the straight line changes near the plait point for the systems cyclohexane-benzene-liquid ammonia and ethylbenzene-styrene-liquid ammonia at 0.0°C. The method of Othmer and Tobias[7] also gives the same results as by Hand plot. When the author's method[8] is used, in which the ratio of the concentration of the diluent in the diluent phase to the concentration of the solvent in the solvent phase against the former concentration is plotted on double logarithmic coordinates, the data in Table II give two straight lines of different slopes, but all other systems satisfy a linear relationship within the range of experimental error.

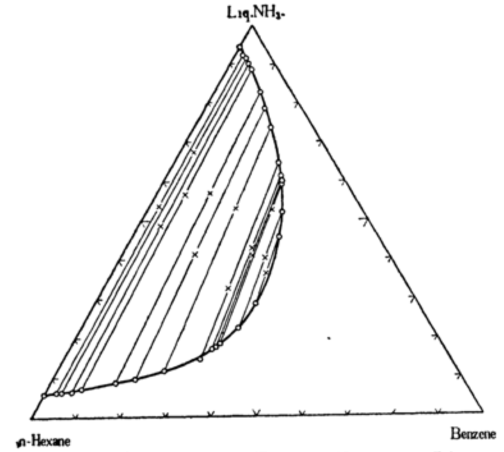

Fig. 1. System *n*-Hexane-Benzene-Liq·NH$_3$ at 20°C, wt. %.

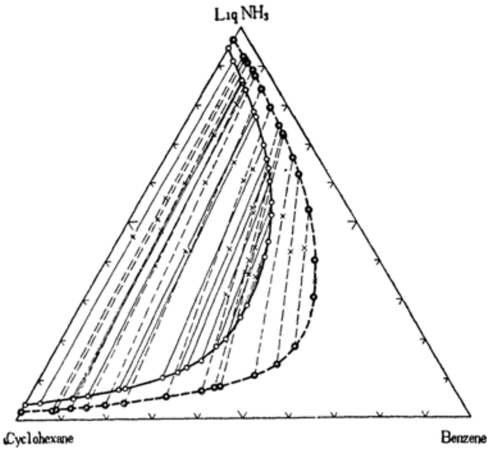

Fig. 2. System Cyclohexane-Benzene-Liq. NH$_3$ at 20°C and 0°C, wt. %.
——○—— 20.0°C
– –◎– – 0.0°C

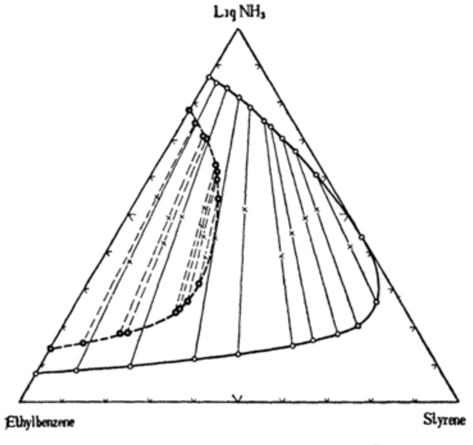

Fig. 3. System Ethylbenzene-Styrene-Liq.NH$_3$ at 0°C and –15.5°C, wt. %.
– –◎– – 0.0°C
——○—— –15.5°C.

Comparison of Solvent Selectivity

There are various measures[1,9,10,11,12,13]:

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5) D. B. Hand, *J. Phys. Chem.*, **34**, 1961 (1930).

6) R. E. Treybal, L. D. Weber and J. F. Daley, *Ind. Eng. Chem.*, **38**, 817 (1946).

7) D. F. Othmer and P. E. Tobias, ibid., **34**, 693 (1942).

8) K. Ishida, This Bulletin, **29**, 956 (1956).

9) K. W. Saunders, *Ind. Eng. Chem.*, **43**, 121 (1951).

10) D. A. Skinner, ibid., **47**, 222 (1955).

11) E. C. Medcalf, A. G. Hill and G. N. Vriens, *Petroleum Refiner*, **30**, No 7, 97 (1951). He used the value at infinite dilution.

12) There are some investigators using the term "separation factor" in the same meaning as the relative distribution ratio, β. For example; B. Weaver, *Anal. Chem.*, **26**, 474 (1954). Usually, β is used for selectivity, e. g., L. F. Crooke, Jr., and M. Van Winkle, *Ind. Eng. Chem.*, **46**, 1474 (1954); A. E. Skrzec and N. F. Murphy, ibid., **46**, 2245 (1954), and so on. See also Ref. 14 and 22.

13) L. Alders, "Liquid-Liquid Extraction", Elsevier Pub. Company, London (1955), p. 85.

TABLE I

EQUILIBRIUM DATA FOR THE SYSTEM *n*-HEXANE-BENZENE-LIQUID AMMONIA AT 20.0°C, WT. %

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)
0.0	—	6.1	—	94.4	—
4.7	53.9	6.5	2.7	92.5	24.6[a]
9.7	67.3	6.6	4.0	91.8	34.0
9.7	48.6	6.6	6.3	90.2	42.7
15.1	56.6	7.1	8.3	88.7	48.6
27.9	56.9	8.8	16.0	82.7	60.0
27.9	41.3	9.6	20.7	78.6	62.8
41.3	52.8	11.7	27.1	73.7	65.0
41.3	32.7	14.8	35.7	64.5	65.9
49.1	42.9	17.2	38.3	61.5	65.6
49.1	40.8	17.8	39.4	60.2	65.5
58.2	52.6	18.8	40.4	59.3	65.3
54.0	40.3	22.7	45.3	52.1	63.2
54.0	36.6	29.0	50.3	45.7	60.0
Plait Point[b]		39.7	56.7	39.7	56.7

a) This value was calculated from the concentrations of ammonia in both layers and the compositions of the total mixture and raffinate.

b) The plait point was estimated according to Treybal et al.[6]

for the comparison of selectivity, but the useful method for comparing the ability of solvents has not been established. It is inconvenient to compare the selectivity of various solvents from the available data by the relative distribution ratio[1,11,12] or the selective power[13], since they are not always constant in the entire separation zone for all ternary systems. Quantitatively, selectivity may be represented more satisfactorily by the selectivity diagram[14] which expresses the relation between y and x, where y is the concentration of the solute in the extract on a solvent-free basis and x is the corresponding concentration in the raffinate. For example, selectivity diagrams for the system cyclohexane-benzene-liquid ammonia at 20°C and 0°C are shown in Fig. 4, a and b, respectively.

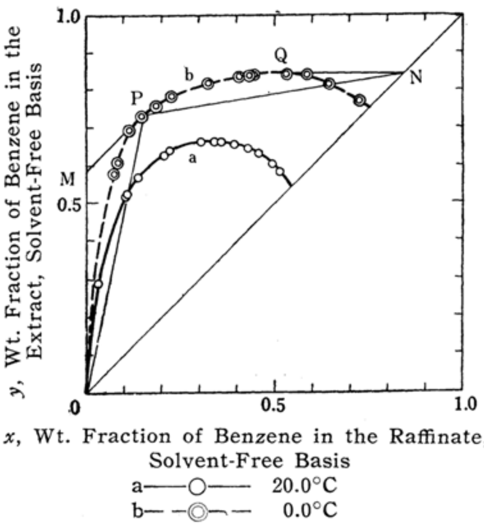

Fig. 4. Selectivity Diagrams for the System Cyclohexane-Benzene-Liq. NH_3, Ammonia as solvent.

If the selectivity I is defined as y-x, then I represents the degree of separation of the solute and the diluent, and is directly related to the selectivity diagram as shown in Fig. 4[15]. The maximum degree of separation of two components in one equilibrium stage is given by $I_{\max}$. The greater the value of $I_{\max}$, the more effective will be the separation. In addition, among solvents having an equal value of $I_{\max}$, the greater the value of $y_{\max}$, where $y_{\max}$ is the maximum concentration of the solute in the extract, the higher will be the purity of the solute obtained by the extraction using that solvent under the given condition. It would be most practical to cmpare the selectivity of solvents by taking account of $I_{\max}$ as well as $y_{\max}$ from the viewpoint of separation of the solute and the diluent. In Fig. 4, $I_{\max}$ on curve b is represented as MO and $y_{\max}$ as the value

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[14] R. E. Treybal, "Liquid Extraction", McGraw-Hill Book Company, Inc., New York (1951), p. 87.

TABLE II

EQUILIBRIUM DATA FOR THE SYSTEM CYCLOHEXANE—BENZENE—LIQUID AMMONIA AT 20.0°C AND 0.0°C, WT. %

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)	NH_3 Wt. %	Benzene Wt. % (Solvent-free Basis)
At 20°C					
0.0	—	4.0	—	94.2	—
5.2	46.2	4.4	3.3	91.4	29.0
16.2	47.8	5.7	10.4	86.2	52.0
28.4	72.3	5.5	10.8	85.7	52.4
44.9	80.1	6.1	13.9	84.0	57.0
28.4	42.3	7.7	20.6	78.2	62.8
44.9	65.4	7.9	22.1	77.1	64.0
56.7	63.4	10.6	30.4	70.0	66.3
44.9	43.2	12.0	33.9	66.0	66.3
54.9	53.6	12.8	35.9	63.8	66.2
44.9	31.6	14.9	39.4	60.1	65.6
52.5	40.1	18.3	43.0	54.8	64.4
52.5	36.9	20.3	45.7	51.4	63.2
54.4	35.8	25.4	49.3	44.9	60.4
56.7	38.7	28.4	51.3	40.8	58.4
Plait Point[b]		34.4	54.8	34.4	54.8
At 0.0°C					
0.0	—	2.1	—	96.8	—
12.4	56.0	2.6	7.2	92.5	58.0
12.4	50.7	2.7	8.2	91.8	60.8
19.0	59.5	2.8	11.3	91.1	69.3
19.0	38.8	3.2	14.7	88.9	73.2
30.4	60.1	3.7	18.4	87.4	75.8
30.4	42.7	4.1	22.9	84.2	78.2
51.0	60.5	5.7	32.3	79.4	81.8
55.1	52.3	7.1	40.5	74.7	83.6
51.0	37.2	7.9	43.5	72.9	83.8
55.1	43.2	8.3	44.8	72.2	84.0
68.4	51.4	10.8	53.1	66.7	84.1
68.4	42.5	13.5	58.9	62.2	84.0
74.1	43.6	18.3	64.3	53.1	81.3
74.1	34.8	30.4	72.8	40.0	77.1
Plait Point[b]		35.5	75.2	35.5	75.2

b) Cf. Table I.

on the ordinate of Q point, and then $I_{\max}\cdot y_{\max}$ would be twice the area of the triangle PON. Therefore, if the maximum separation factor is defined by the value of $I_{\max}\cdot y_{\max}$, it will be indicated by the definite value of $I_{\max}\cdot y_{\max}$ between 1.0 in the most ideal case, and zero with no effectiveness for the separation. This will be used as the convenient measure of comparison for selectivity.

Values of $I_{\max}\cdot y_{\max}$ calculated from the available data of ternary systems with liquid ammonia as one component are given in Table IV. In order to compare with other solvents, the values of $I_{\max}\cdot y_{\max}$ of representative solvents, which have been used or may be used as a solvent for the separation of hydrocarbons, are listed in the order of magnitude.

There are many factors other than selectivity which must be considered in choosing a solvent for a liquid extraction process, and it is evident that solvent power is the most important factor among them. In general, the amount of solvent in the raffinate phase is small and the large amount of solvent for recovery is carried in the solvent phase. If the diluent and the solute are to be separated as far as possible, a major amount of

TABLE III

EQUILIBRIUM DATA FOR THE SYSTEM ETHYLBENZENE STYRENE-LIQUID AMMONIA AT 0.0°C AND −15.5°C, WT. %

Total Mixture		Hydrocarbon Layer		Solvent Layer	
Styrene Wt. % (Solvent-free Basis)	NH_3 Wt. %	NH_3 Wt. %	Styrene Wt. % (Solvent-free Basis)	NH_3 Wt. %	Styrene Wt. % (Solvent-free Basis)
At 0.0°C					
0.0	—	14.1	—	78.1	—
9.1	54.8	15.7	8.1	74.7	11.7
19.0	49.0	18.3	17.3	71.1	23.0
20.7	42.3	18.4	19.2	70.5	26.2
34.4	51.9	24.0	31.5	63.4	36.9
34.9	46.8	24.8	32.5	61.7	38.2
36.1	44.0	27.0	34.5	59.5	38.5
38.0	38.9	31.5	37.2	54.3	40.2
Plait Point[b]		47.0	41.2	47.0	41.2
At −15.5°C					
0.0	—	8.0	—	87.0	—
10.5	37.3	8.5	9.9	85.2	16.5
25.0	49.4	9.6	23.0	83.9	34.3
40.6	43.8	11.4	39.0	81.4	51.5
53.3	51.4	12.7	50.2	78.8	62.4
66.3	39.0	15.1	64.8	75.1	73.7
72.0	45.1	16.6	70.2	73.6	78.0
79.8	49.0	18.2	77.4	70.3	84.0
86.4	51.2	20.3	84.2	66.8	89.3
93.2	41.3	26.5	92.8	60.4	94.9
100.0	—	43.9[c]	—	43.9[c]	—

b) Cf. Table I.

c) Since −15.5°C is the upper critical solution temperature for the binary mixtures of styrene and liquid ammonia, the concentration of ammonia was estimated from the composition at the critical point.

solvent should be recovered at the end of the enriching section of the extraction tower where the extract is obtained. Therefore, the amount of other components dissolved in that solvent, (1−$Sy_{\max}$), where $Sy_{\max}$ is the concentration of the solvent in the solvent phase at $y_{\max}$, will be an index of solvent power of that solvent. This value is given in the column 8 and the product of that value and $I_{\max}\cdot y_{\max}$ is given in column 9 in Table IV, as a comprehensive index.

As will be clear from Table IV, liquid ammonia is a poor solvent for the separation of paraffins and naphthenes[3,26], but for the separation of C_6–C_7 saturated hydrocarbons and aromatics or olefins, it is comparable to diethyleneglycol, better than liquid sulfur dioxide with respect to the selectivity and the solvent power. As ammonia has relatively high vapor pressure, it is comparatively easy to separate liquid ammonia from other components. And also, its extensive use as a mixed solvent is possible because of miscibility with water, lower alcohols, amines, and esters[1,27]. Considering the close relationship between the production of ammonia and the petrochemical industry, it is thought that there is a possibility of the use of liquid ammonia as a solvent for the separation of hydrocarbons.

Summary

Equilibria for the systems *n*-hexane-benzene-liquid ammonia (20°C), cyclohexane-benzene-liquid ammonia (20°C and 0°C), and ethylbenzene-styrene-liquid ammonia (0°C and −15.5°C) were determined. It was shown that the ability of a solvent would be most practically compared by the product of the maximum

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[26] A. W. Francis, ibid., **36**, 764 (1944).

[27] U. S. Pat. 2,721,164 (Oct. 18, 1955), *C. A.*, **50**, 2968c (1956); U. S. Pat. 2,723,940 (Nov. 15, 1955), *C. A.*, **50**, 3748d (1956).

TABLE IV

SELECTIVITIES AND CAPACITIES OF SOLVENTS FROM VARIOUS SYSTEMS

Components			Temp. °C	I_{max} Wt. Fraction	y_{max} Wt. Fraction	$I_{max} \cdot y_{max} \times 10^2$	$1\text{-}Sy_{max}$ Wt. Fraction	$I_{max} \cdot y_{max} \times (1-Sy_{max}) \times 10^2$	Ref.
Diluent	Solute	Solvent							
n-Hexane	Methylcyclopentane	Aniline	34.5	0.115	1.00	11.5	0.515	5.9	16
〃	Cyclohexane	Liq. NH_3	20	0.055	1.00	5.5	0.058	0.3	3
n-Heptane	〃	Furfural	30	0.135	1.00	13.5	0.139	1.9	17
〃	〃	Aniline	25	0.097	1.00	9.7	0.262	2.5	18
n-Hexane	Benzene	Ethylenediamine	20	0.615	0.848	52.1	0.225	11.7	19
〃	〃	SO_2	−28.9	0.61	0.68	41.5	0.15	6.2	20
〃	〃	Liq. NH_3	20	0.443	0.659	29.2	0.355	10.4	
Cyclohexane	〃	β,β′-Thiodipropionitrile	Room temp.	0.765	0.96	73.1	0.30	21.9	9
〃	〃	Liq. NH_3	0	0.585	0.842	49.3	0.333	16.4	
〃	〃	〃	20	0.433	0.664	28.8	0.300	8.6	
〃	〃	Nitromethane	25	0.375	0.588	22.1	0.29	6.4	21
n-Heptane	〃	Diethyleneglycol	25	0.686	1.00	68.6	0.313	21.5	22
〃	〃	92%-Diethyleneglycol-8% H_2O	125	0.56	1.00	56.0	0.285	16.0	22
〃	〃	SO_2	−28.9	0.63	0.73	46.0	0.16	7.3	20
〃	〃	Furfural	Room temp.	0.38	0.592	22.5	0.335	7.5	9
Methylcyclohexane	Toluene	Liq. NH_3	21.1	0.38	0.73	27.75	0.35	9.7	1
n-Heptane	〃	β,β′-Thiodipropionitrile	25	0.715	1.00	71.5	0.296	21.2	10
〃	〃	Liq. NH_3	−7.5	0.595	1.00	59.5	0.575	34.2	8
〃	〃	〃	0	0.668	0.955	64.8	0.418	27.1	2,8
〃	〃	〃	−15	0.556	1.00	55.6	0.268	14.9	8
〃	〃	Diethyleneglycol	25	0.490	1.00	49.0	0.17	8.3	10
〃	〃	SO_2	−28.9	0.66	0.73	48.2	0.14	6.8	20
〃	〃	Liq. NH_3	20	0.468	0.808	37.8	0.306	11.6	2,8
〃	〃	Aniline	25	0.290	0.470	13.6	0.266	3.6	13
〃	〃	97%-Acetic acid-3% H_2O	23	0.19	0.55	10.5	0.69	7.2	23
n-Heptane	Octene-1	Liq. NH_3	20	0.115	1.00	11.5	0.063	0.7	3
〃	〃	〃	0	0.108	1.00	10.8	0.032	0.3	3
Decalin	Tetralin	〃	20	0.415	1.00	41.5	0.136	5.6	24
〃	〃	〃	0	0.323	1.00	32.3	0.063	2.0	24
Ethylbenzene	Styrene	〃	−15.5	0.126	1.00	12.6	0.561	7.1	
〃	〃	Diethyleneglycol	25	0.103	1.00	10.3	0.271	2.8	25
〃	〃	Liq. NH_3	0	0.068	0.412	2.8	0.51	1.4	

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15) K. Ishida, *Science Repts. Research Inst. Tohoku Univ.*, Ser. A, **5**, 377 (1953).

16) B. DeB. Darwent and C A. Winkler, *J. Phys. Chem.*, **47**, 442 (1943).

17) E. N. Pennington and S. J. Marwil, *Ind. Eng. Chem.*, **45**, 1371 (1953).

18) T. G. Hunter and T. Brown, ibid., **39**, 1343 (1947).

19) A. P. C. Cumming and F. Morton, *J. Appl. Chem.*, **3**, 358 (1953).

20) C. N. Satterfield, J. H. Powell, Jr., E. A. Oster, Jr., and J. P. Noyes, *Ind. Eng. Chem.*, **47**, 1458 (1955).

21) H. I. Weck and H. Hunt, ibid., **46**, 2521 (1954).

22) G. C. Johnson and A. W. Francis, ibid., **46**, 1662 (1954).

23) D. F. Othmer and P. E. Tobias, ibid., **34**, 690 (1942).

24) K. Ishida, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **60**, 864 (1957).

25) M. G. Boobar, P. M. Kerschner, R. T. Struck, S. A. Herbert, N. L. Gruver and C. R. Kinney, *Ind. Eng. Chem.*, **43**, 2922 (1951).

value of selectivity and the maximum concentration of the solute in the extract, i. e. maximum separation factor. Selectivity and solvent power of some solvents were compared by this definition and it was recognized that liquid ammonia is comparable to diethyleneglycol as a solvent for the separation of saturated hydrocarbons and aromatic or olefinic hydrocarbons, rather than liquid sulfur dioxide.

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