# RECOMMENDED TEST MIXTURES FOR DISTILLATION COLUMNS

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Second Edition

THE INSTITUTION OF CHEMICAL ENGINEERS
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# FOREWORD TO THE FIRST EDITION

The European Federation of Chemical Engineering is a non-profit making association of technical and scientific societies which are concerned with chemical engineering, chemical technology and process engineering. Its object is to promote European co-operation in these fields. The Federation has set up a number of Working Parties for dealing with particular subjects. A Working Party on Distillation was set up in 1963 and in 1968 its terms of reference were extended to cover, in addition, Absorption and Extraction. As part of its effort to promote European co-operation in the field of distillation, the Working Party has already published a "Six-Language Vocabulary of Distillation Terms" (English, French, German, Italian, Spanish, Russian).

One of the main activities of the Working Party has been the organisation of informal discussion meetings, which have been devoted to various subjects in the field of distillation. These meetings have been attended by the Working Party members and a number of specially invited participants with particular interests in the subject under discussion. So far seven such meetings have proved most valuable in establishing personal contacts between experts with similar interests and in defining the state of progress in various fields of distillation.

At several of these meetings the view was expressed that the situation concerning the use of test mixtures in the determination of equipment parameters was quite unsatisfactory. It was therefore decided to attempt a standardisation of test mixtures, mainly based on literature data but supplemented where possible with unpublished data and experimental work. With this aim the Working Party set up in late 1966 a Sub-Committee with Mr. F. J. Zuiderweg of Koninklijke/Shell-Laboratorium, Amsterdam as Chairman and Professor S. R. M. Ellis of Birmingham University and Dr. H. -W. Brandt of Farbenfabriken Bayer AG, Leverkusen as the other members.

After a preliminary study, the Sub-Committee drew up a list of recommended test mixtures and standardised methods of inspection of

the equilibrium data, physical constants and other required information. After approval by the Working Party members, the Chairman of the Sub-Committee sought and obtained the co-operation of University and industrial workers in various European countries and the U.S.A. for collection and screening of the required literature data.

At about the same time that the need for standardization of test mixtures was recognized by the Working Party, a parallel development was taking place within the Fachausschuss "Thermische Zerlegung von Gasund Fluessigkeitsgemischen" der Verfahrenstechnischen Gesellschaft im Verein Deutscher Ingenieure (VDI) under the Chairmanship of Professor Dr. H. Glaser of the University of Stuttgart. Discussions took place with the very gratifying result that a full-hearted co-operation between the Working Party Sub-Committee and the VDI group was established.

The preparation of this manual has involved a large amount of work. The enthusiastic co-operation of the large number of workers in this truly international effort is gratefully acknowledged. A full list of the people who have participated in the work is given in the Introduction of Mr. F. J. Zuiderweg, which follows this Foreword and which also sets out the general principles on which the work was based. Special thanks are due to Mr. F. J. Zuiderweg for organising the work of the Sub-Committee, to Professor Dr. H. Glaser for making available a literature survey on the test mixtures, which has been carried out at the Institut fuer Technische Thermodynamik of the University of Stuttgart, to Dr. K. Sigwart for arranging for redetermination of a large number of physical data in the A.P. division of Farbenfabriken Bayer A. G., Leverkusen and to Koninklijke/Shell-Laboratorium, Amsterdam, for assistance in preparing the final manuscript for printing.

A. J. V. Underwood
Chairman
Working Party on Distillation, Absorption and Extraction of the
European Federation of Chemical Engineering.

# FOREWORD TO THE SECOND EDITION

The first edition of the manual "Recommended Test Mixtures for Distillation Columns" was issued in 1969. Since that time, the Manual has been used by a large number of investigations for studies of the mass-transfer performance of distillation equipment. However, in the course of the years it became apparent that more information was needed on the thermodynamic properties of the mixtures and that — because of toxicity — the test mixtures containing benzene are not permitted to be used in the laboratory any more. Therefore, the Working Party "Distillation, Absorption and Extraction" concluded that an attempt should be made to issue a second, revised edition of the Manual. Professor Dr. rer. nat. U. Onken of Dortmund University, Germany, was found willing to act as editor-in-chief for the revision.

The Working Party has much pleasure to present herewith the second and revised edition of the Manual "Recommended Test Mixtures for Distillation Columns". Many thanks are due to Professor U. Onken for his continuous effort to bring the project to completion, to Dr. H. W. Brandt of the former AP division of Bayer AG for the stimulation and assistance in the collection of data, and to Dr. W. Arlt of Bayer AG for his important contribution in completing and editing the manuscript.

F. J. Zuiderweg
Chairman
Working Party on Distillation, Absorption and Extraction of the
European Federation of Chemical Engineering.

# INTRODUCTION

This second edition of the manual of test mixtures for testing distillation columns contains data for twelve systems. As already stated in the preface, the three systems containing benzene have been excluded because of health hazards. Out of these systems two have been replaced by new systems with similar separation factor and boiling temperatures, i.e. benzene/toluene by toluene/chlorobenzene and benzene/*n*-heptane by cyclohexane/*n*-heptane. One system (benzene/1,2-dichlorobenzene) was dropped, because the system *n*-heptane/methylcyclohexane has approximately the same separation factor, and boiling temperatures are less than 20 K higher.

From the systems for vacuum distillation, 2-methylnaphthalene/1-methylnaphthalene was dropped, because available original data appeared to be unreliable. Instead of the methylnaphthalene system *o*-chlorotoluene/*p*-chlorotoluene with a similarly low separation factor is now included.

For pressure distillation, data for an additional system are given, i.e. propene/propane. As a system with high surface tension and high heat of vaporization methanol/water has been included, thus bringing up the number of systems in this edition to twelve.

Of predominant importance in testing distillation columns is the quality of equilibrium data. Therefore for this new edition carefully selected and scrutinized vapour-liquid equilibrium data and also vapour pressures available from the Dortmund Data Bank (DDB) have been used. Of course, the original experimental data were correlated with the aid of a thermodynamic model equation; from the equations available in the DDB (Margules, van Laar, Wilson, NRTL, UNIQUAC) the Wilson equation was used for those systems showing a deviation from Raoult's law. Besides equilibrium data, for each isobaric data set a correlation for the relative volatility is given.

As to physical properties, in this edition information on additional properties, as far as reliable data were available, is presented,

i.e. refractive index, viscosity, critical temperature and second virial coefficient of pure components, densities of mixtures and mixing enthalpies. Besides, information on safety has been increased in this edition. And of course, needless to say, all information has been upgraded to the present level of knowledge, including methods of analysis and purification procedures.

This second edition of the distillation test mixture manual could not have been accomplished without the help of many workers. First cand. ing. J. Schomschor (Department of Chemical Engineering, University of Dortmund) has to be mentioned; he performed the major part of the large amount of calculations which were necessary for the tables.

The task of editing was considerably alleviated by the fact that after the first edition other publications on test mixtures have appeared. In 1977 a report on "Reference Materials for Testing Distillation Columns" was published by the National Physical Laboratory, Teddington, Middlesex, U.K.; author E. F. G. Herington. The permission to use the results of this report for the new edition of the test mixture manual is gratefully acknowledged. Likewise thanks are due to G. J. Keller, Fractionation Research Inc., South Pasadena, Cal., USA, for supplying data from his organization for the systems propene/propane and *i*-butane/*n*-butane. Finally, K. Stephan and H. Hildwein have to be thanked; their compilation of "Recommended Data of Selected Compounds and Binary Mixtures" has been very useful for preparing this edition of distillation test mixtures. The data compilation of K. Stephan and H. Hildwein has been supported by the "Arbeitsgemeinschaft Industrieller Forschungsvereinigungen e.V. (AIF)". Unluckily only eight of the 14 systems of that project belong to the twelve distillation test mixtures recommended by the EFCE Working Party.

Assistance and recommendations to this project have been given by many colleagues. E. Hala (Czechoslovak Academy of Science, Prague) has supported the efforts by performing measurements of the vapour pressures of *o*- and *p*-chlorotoluene as a basis for the vapour-liquid equilibrium data. Several colleagues supplied useful recommendations; of these W. Meier (Sulzer, Winterthur, Switzerland) and R. J. P. Brierley (ICI, Billingham, U.K.) should be mentioned in particular.

# SYSTEMS STUDIED

| System | Pressure mbar | Number of theoretical Plates | Page |
|---|---|---|---|
| 1. *n*-Heptane/Methycyclohexane | 1013 | 20– | 11 |
| 2. Toluene/Chlorobenzene | 1013 | 3–7 | 14 |
| 3. Cyclohexane/*n*-Heptane | 1013 | 3–7 | 17 |
| 4. Methylcyclohexane/Toluene | 1013 | 5–11 | 20 |
| 5. Methanol/Water | 1013 | 1–4 | 23 |
| 6. *p*-Xylene/*m*-Xylene | 1013<br>400<br>200<br>100<br>50<br>30 | 50–250 | 26 |
| 7. Chlorobenzene/Ethylbenzene | 1013<br>400 | 16–40 | 31 |
| | 200<br>100<br>50<br>30 | 10–22 | |
| 8. *trans*-Decalin/*cis*-Decalin | 200<br>100<br>50<br>30<br>15<br>7.5 | 5–15 | 37 |