HETEROGENEOUS EQUILIBRIUM OF CONDENSED GAS—VAPOR APROTONIC
SOLVENTS AND ELECTROLYTES BASED ON THEM.
I. INDIVIDUAL SOLVENTS

I. L. Gaidym, I. G. Gurevich,
V. K. Shchitnikov, V. S. Dubasova,
and B. I. Tumanov

The results of an experimental determination of the saturated-vapor pressure of organic solvents and electrolytes based on them are presented, and used to calculate the thermodynamic characteristics of the vaporization process.

As noted in [1], interest arising in electrochemical energetics regarding a definite group of organic solvents has led to their use for the preparation of electrolytes for a relatively new class of chemical current sources, with an anode of alkali metals, primarily lithium [2]. These sources, which have considerably larger power capacity than the primary elements and accumulators that are widely used at present, are intended for operation over a broad temperature range [3]. At the same time, in view of their specificity, they must be hermetic devices structurally, preventing any contact of their contents with moisture in the surrounding medium. These two factors necessitate a knowledge of the saturated-vapor pressure of the given electrolytes, especially as some of the solvents used are low-boiling.

As a result, such data has not yet been included in reference handbooks, while the information appearing in scientific periodicals is partial and fragmentary in character, and refers to individual solvents [4, 5], whereas in practice it is their mixtures which are presently of interest, since such mixtures permit more complete satisfaction of the complex of requirements imposed on the given electrolyte. In addition, the vapor pressure of individual solvents is measured by different methods. As regards the vapor pressure of the electrolyte, such data are generally missing, to the best of our knowledge. These were the considerations which, taken together, stimulated the present work.

Of the small group of materials which are used in practice at present for the given class of current sources, the following were chosen for the investigation: propylene carbonate (PC), γ-butyrolactone (γ-BL), tetrahydrofuran (THF), 1,2-dimethoxyethane (1,2-DMOE), and their mixtures. Lithium perchlorate ($LiClO_4$) was adopted as the ionogenic component of the electrolyte.

In conducting the experiment, of course, particular attention was paid to the purity of the experimental samples and primarily to their water content. In the initial γ-BL of pure grade, the total impurity content was 0.4% and the water content 0.14%; in PC, the corresponding figures were 0.25 and 0.3%.

Purification of PC was performed by double distillation under vacuum (∿3 mm Hg) at a temperature of 359-360°K, while vacuum rectification was used for γ-BL. Purification of THF and 1,2-DMOE of pure grade was performed in the phosphoorganic-compound laboratory of the chemistry faculty at Moscow State University. After preliminary breakdown of peroxides, the solvents were boiled with solid NaOH, distilled, and boiled with metallic sodium and then with sodium rolled with powdered benzophenone. After the appearance of a blue coloration, the solvent was distilled and charged with zeolite of type 4 Å.

The moisture content in all the purified solvents, determined by the Fisher method, was $(5-7) \cdot 10^{-3}\%$.

Lithium perchlorate of pure grade was dried for 20 h under vacuum at 397°K.

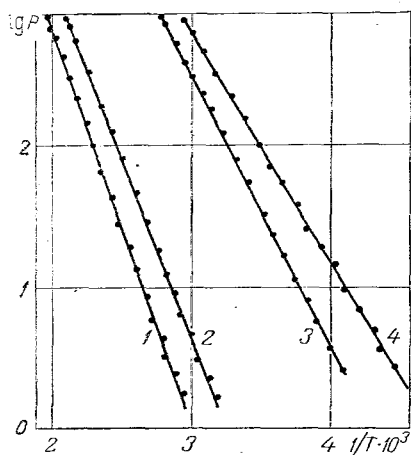Fig. 1.   Fig. 2.

Fig. 1.   Temperature dependence of the saturated-vapor pressure P
(mm Hg) of the individual solvents: 1) PC; 2) γ-BL; 3) 1,2-DMOE;
4) THF.

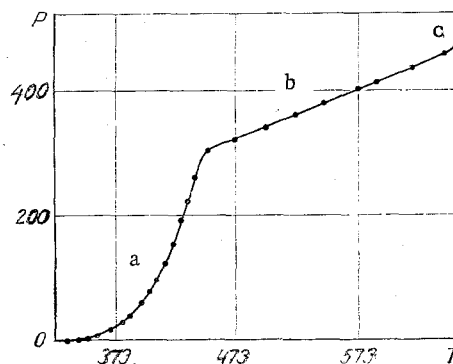Fig. 2.   Temperature dependence of the vapor pressure P of γ-BL in
the region of: a) saturated vapor; b) unsaturated vapor; c) ther-
mal decomposition.

Electrolyte solutions were prepared in a hermetic box in an atmosphere of dry argon.
The moisture content in the final electrolyte was $(1.8-3.5) \cdot 10^{-2}\%$.

Samples prepared in this way were sealed into glass ampuls.

The vapor pressure of the solvents and the electrolytes based on them was measured by a
static method with a membrane null-manometer, which has a series of advantages in comparison
with other methods [6].   The high volatility and hygroscopicity of the initial compounds
necessitated the development of a special procedure for filling the membrane chamber, elimi-
nating the possibility of contact between the experimental sample and the surrounding medium.
In this procedure, the glass ampul with the sample in an atmosphere of "dry" argon was con-
nected to a special "manifold," made of glass and having several capillary tubes for the re-
moval of samples.   After the creation of vacuum ($\sim 10^{-2}$ mm Hg), the ampul was broken and the
material was distilled into the capillaries; in the case of a multicomponent system, the mate-
rial was decanted into the capillaries without distillation.   Filling of the null-manometer
membrane chamber with material from the capillary tubes of the "manifold" was performed anal-
ogously, using a glass T joint.

After filling, the membrane chamber was placed in a thermostat and the vapor pressure
was measured with the temperature rising and falling.   The pressure was measured by a MChR-3
mercury manometer with an accuracy of ±0.1 mm Hg and the temperature by glass thermometers
with scale divisions of ±0.1°C.

The experimental vapor-pressure data for THF, PC, γ-BL, and 1,2-DMOE in the given tem-
perature range are well approximated by a linear dependence log P = f(1/T) (Fig. 1).   The
temperature dependence of the saturated vapor pressure is used to calculate the mean values
of the entropy and enthalpy of the vaporization process of the given solvents, which are
given in Table 1, together with values of the constants in the equation log P = A − B/T
approximating this dependence.   All these quantities are determined with a confidence level
of 0.95 from experimental data treated by the least-squares method.

The thermodynamic characteristics obtained in the present work for the vaporization of
THF, PC, and 1,2-DMOE are in good agreement with the literature data [4, 5, 7].   For γ-BL,
these characteristics have not been previously obtained.   The boiling points of the pure
solvents (except for PC) also correspond with the literature data.

Table 2 shows the thermodynamic characteristics of the vaporization of an electrolyte
(1 M LiClO₄ solution) based on the given solvents.   The temperature dependence of the satu-
rated-vapor pressure for these electrolytes is also well described by the equation given

TABLE 1. Thermodynamic Characteristics of the Vaporization of Tetrahydrofuran, γ-Butyrolactone, 1,2-Dimethoxyethane, and Propylene Carbonate

Solvent	Temperature range, °K	ΔH_T^0, kJ/mole	ΔS_T^0, J/mole·°K	B.p.,* °K	lg $P = A - \dfrac{B}{T}$	
					A	B
THF	238—340	31,31±0,56	92,40±1,71	339,05	7,70±0,08	1634±29
γ-BL	325—475	49,07±0,44	103,41±1,32	475,20	8,27±0,06	2561±28
1,2-DMOE	234—358	36,80±1,02	103,20±3,12	357,45	8,26±0,14	1923±53
PC	340—515	53,46±1,15	104,96±3,05	509,35	8,36±0,15	2791±55

*At atmospheric pressure.

TABLE 2. Thermodynamic Characteristics of the Vaporization of 1 M LiClO₄ Solution in Aprotonic Solvents

Solvent	Temperature range, °K	ΔH_T^0, kJ/mole	ΔS_T^0, J/mole·°K	B.p.,* °K	lg $P = A - \dfrac{B}{T}$	
					A	B
THF	231—342	31,61±0,46	92,94±1,55	340,25	7,73±0,08	1650±24
γ-BL	324—481	47,39±0,61	98,72±1,46	480,45	8,03±0,07	2474±31
1,2-DMOE	233—358	32,20±0,55	89,89±1,80	358,25	7,57±0,09	1680±28

*At atmospheric pressure.

above. The poor solubility of lithium perchlorate did not permit the influence of the electrolyte concentration on the given process to be investigated (concentrations below 1 M are of no practical interest).

Comparison of the thermodynamic characteristics of the vaporization of the solvents considered here, and electrolytes based on them, shows that they are very little changed by the presence of one mole of lithium perchlorate. Thus, it may be noted that the boiling points of the electrolytes are 2-5°K higher than the boiling points of the corresponding solvents. As for the reduction in saturated-vapor pressure of the electrolyte in comparison with the vapor pressure of the corresponding solvent, this rises with increase in temperature, reaching values of 25-30, 90-100, and 8-10 mm Hg, respectively, for THF, γ-BL, and 1,2-DMOE at the upper limit of the experimental temperature range (in the electrolyte based on 1,2-DMOE, the vapor pressure somewhat exceeds the vapor pressure of the pure solvent at low temperatures).

Note, in conclusion, that the saturation-vapor pressure of solvents in the unsaturated-vapor region has been studied within the framework of a static method, which allowed values of their molecular mass and the temperature of onset of decomposition to be calculated. As an example, the results of studying the temperature dependence of the pressure for γ-BL are shown in Fig. 2. The exponential portion of the curve (section a) corresponds to saturated vapor, while section b corresponds to the region of the unsaturated state and section c (a vertical line) to the process of thermal decomposition of γ-BL (653°K). By an analogous method, the temperature of onset of thermal decomposition was measured for THF (623°K), PC (533°K), and 1,2-DMOE (583°K).

Using data on the membrane-chamber volume, the temperature of complete vaporization, the vapor pressure, and the amount of material, the molecular masses of the given solvents were calculated; within the limits of measurement error ($\sim 1\%$), they coincided with those calculated from their chemical formula.

NOTATION

p, saturated-vapor pressure, mm Hg; T, temperature, °K; ΔH, heat of vaporization, kJ/mole; ΔS, change in entropy, J/mole·°K.

LITERATURE CITED

1. I. G. Gurevich, K. B. Gisina, V. K. Shchitnikov, et al., "Viscosity and density of aprotonic solvents and electrolytes based on them," Inzh.-Fiz. Zh., 42, No. 3, 422-427 (1982).
2. S. I. Zhdanov and Yu. M. Povarov, "Chemical current sources with electrolytes based on organic solvents," in: Results of Science and Engineering. Electrochemistry [in Russian], Vol. 9, VINITI, Moscow (1974), pp. 46-153.
3. L. Z. Khil'kevich, "Chemical current sources based on new electrochemical systems," in: Results of Science and Engineering. Generators of Direct Conversion of Thermal and Chemical to Electrical Energy [in Russian], Vol. 5, VINITI, Moscow (1979), pp. 47-84.
4. G. K. Borisov and S. G. Chugunova, "Saturated-vapor pressure and density of tetrahydrofuran," Zh. Fiz. Khim., 50, No. 11, 3004 (1976).
5. E. I. Shcherbina, "Molecular interactions and laws of selective separation of hydrocarbon mixtures of binary solvents," Author's Abstract of Doctoral Dissertation, Moscow (1979).
6. A. V. Suvorov, Thermodynamics of the Vapor State [in Russian], Khimiya, Leningrad (1967).
7. A. J. Gordon and R. A. Ford, Chemist's Companion, Wiley (1973).