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VISCOSITY AND DENSITY OF APROTONIC SOLVENTS
AND ELECTROLYTES BASED ON THEM

I. G. Gurevich, K. B. Gisina,   UDC 532.13:532.14:541.135
V. K. Shchitnikov, V. S. Dubasova,
and V. L. Nikonov

The results of an experimental determination of the viscosity and density of organic solvents and electrolytes based on them are given.

Organic solvents are widely used in applied chemistry. Interest has recently been shown in them in electrochemical power engineering, where these nonaqueous solvents are used to produce an electrolyte for current sources in which alkali metals, primarily lithium, are used as the anodic material [1].

Research on the design of such current sources has led to a fairly precise specification of the indices that determine the suitability of these solvents [2]. It is difficult, however, to find substances that directly satisfy the whole set of requirements and this has led to the use of electrolytes that employ not individual substances, but mixtures, in which the drawbacks of some solvents are compensated by the advantages of others.

An index of particular importance is the viscosity, since it has an appreciable effect on the electrical conductivity of the electrolyte and diffusion transfer in it, which ultimately affects the output parameters of the current source.

Unfortunately, the reference literature usually provides no data for solvents of practical interest, while data found in periodicals is of a specific and fragmentary nature, and in most cases relate to individual solvents [3, 4] — data for mixtures have only recently begun to appear [5]. These circumstances stimulated the present investigation.

For the considered class of current sources interest is now confined to a relatively small group of substances, which includes such solvents as propylene carbonate (PC), γ-butyrolactone (γ-BL), tetrahydrofuran (THF), and mixtures of these. As regards the electrolyte, lithium perchlorate ($LiClO_4$) is one of the compounds used for its preparation. The results of an investigation of their properties are given below.

The purity of the samples used for the investigation was ensured by the high purity of the initial substances (these were usually "pure" grade, in which the total impurity content

TABLE 1. Values of Constants Contained in Equations. (1) and (2) Approximating the Temperature Dependences of the Viscosity and Density of Aprotonic Solvents and Electrolytes Based on Them*

Solvent, electrolyte	$\mu_\infty \cdot 10^4$, N·sec/m²	E_μ, kJ/mole	E_μ/R, °K	$d_0 \cdot 10^{-3}$, kg/m³	$\beta_0 \cdot 10^3$, 1/deg
Propylene carbonate (PC)	0,145±0,009	12,73±0,61	1532±74	1,224±0,003	0,798±0,021
γ-Butyrolactone (γ-BL)	0,211±0,005	10,40±0,22	1252±27	1,149±0,001	0,820±0,010
Tetrahydrofuran (THF)†	0,243±0,010	7,34±0,18	883±22	0,906±0,004	1,090±0,037
PC:THF (1:1)	0,339±0,024	7,93±0,86	954±104	1,066±0,004	0,704±0,047
PC:THF (7:3)	0,253±0,010	9,65±0,36	1161±43	1,127±0,010	0,520±0,087
γ-BL:THF (1:1)	0,283±0,004	8,14±0,14	979±17	1,033±0,005	0,873±0,063
γ-BL:THF (7:3)	0,291±0,009	8,70±0,28	1047±34	1,079±0,003	0,676±0,036
1 M LiClO₄ in PC	0,056±0,005	17,2 ±0,89	2070±107	1,280±0,005	0,723±0,036
1 M LiClO₄ in γ-BL	0,104±0,006	14,39±0,49	1731±59	1,209±0,004	0,702±0,030
1 M LiClO₄ in THF	0,202±0,005	9,22±0,46	1109±55	1,059±0,058	3,048±1,380
1 M LiClO₄ in PC:THF (1:1)	0,360±0,015	9,74±0,42	1172±51	1,122±0,007	0,442±0,076
1 M LiClO₄ in PC:THF (7:3)	0,135±0,011	13,64±0,82	1641±99	1,194±0,005	0,563±0,046
1 M LiClO₄ in PC:THF (1:1)	0,281±0,018	10,21±0,70	1228±84	1,098±0,010	0,519±0,122
1 M LiClO₄ in γ-BL:THF (7:3)	0,195±0,011	11,70±0,61	1408±74	1,142±0,005	0,545±0,050

*The volume composition of the solvent mixtures is given.
†The theoretical relations were obtained with the aid of the data of [3].

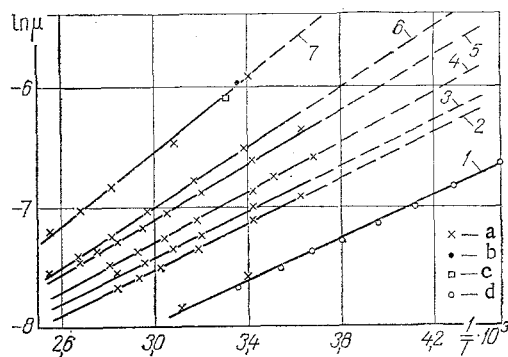Fig. 1. Temperature dependence of viscosity μ (N·sec/m²) of aprotonic solvents and mixtures of them: 1) THF; 2) γ-BL:THF (1:1); 3) PC:THF (1:1); 4) γ-BL:THF (7:3); 5) PC:THF (7:3); 6) γ-BL; 7) PC. a) Our experimental data; b) data of [4]; c) data of [5]; d) data of [3].

was 0.25-0.4%; the moisture content was 0.14-0.3%) and by further dehydration by distillation under vacuum. The moisture was removed from THF by a more complex technique. "Pure"-grade lithium perchlorate was dried for 20 h under vacuum at 160°C. The electrolyte solutions were prepared in a sealed box in a dry argon atmosphere. The moisture content of the prepared electrolytes was $(1.8-3.5) \cdot 10^{-2}\%$.

To measure the viscosity we used a VPZh capillary viscometer. The density of the investigated substance, which is required for calculation of the viscosity, was determined by a pycnometer. The viscometer and pycnometer were submerged in a glass bath in which the temperature was controlled to an accuracy of ±0.1°K, which enabled us to investigate the temperature dependences of the viscosity and density at temperatures 273-393°K (the upper temperature limit for the individual solvents and mixtures containing them was determined by the boiling point). The viscosity measurements at each temperature were repeated 5-7 times.

The temperature dependence of the viscosity of the investigated solvents and electrolyte solutions based on them was approximated by the known exponential law [6]:

$$\mu = \mu_\infty \exp [E_\mu/RT], \tag{1}$$

where μ_∞ is a const; R is the gas constant.

Table 1 gives the values of the constants in (1), at the 0.95 confidence level, from experimental data treated by the least-squares method for all the investigated liquids. This table also gives the values of the constants contained in the equation expressing the temperature dependence of the density of the investigated substances:

$$d = d_0 (1 - \beta_0 \Delta T), \tag{2}$$

where β_0 is the cubic expansion coefficient at T_0; $\Delta T = T - T_0$; in the treatment of the experimental data 273°K was taken as T_0.

It should be noted that most of our results are in good agreement with the available sparse data of other authors [3-5] (Fig. 1).

Of the investigated solvents the most viscous with the highest activation energy is propylene carbonate, followed by γ-butyrolactone and tetrahydrofuran (the last substance is much less viscous; its activation energy is approximately half of that of propylene carbonate). The viscosities of binary mixtures of these solvents lay between the viscosities of the individual components (Fig. 2); a plot of the viscosity of a mixture against its composition gave a curved line. It is of interest to note that for the composition X:THF (1:1) and lower (as regards the first component), where X is PC or γ-BL, the effects of the first components are practically the same: The viscosities of the solutions are close in absolute values and in activation energies. When the composition is altered by an increase in concentration of
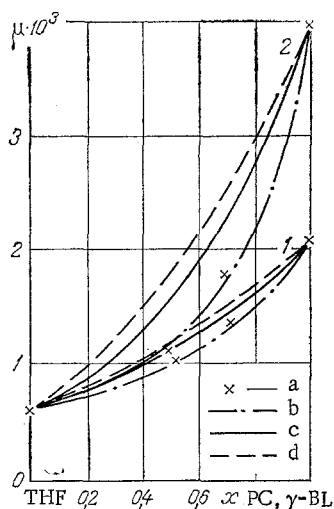
Fig. 2   Fig. 3

Fig. 2. Plots of viscosity μ (N·sec/m²) of solvent mixture against mole (volume) fraction (x, $\bar{x}$) of variable component (T = 273°K): 1) γ-BL:THF; 2) PC:THF. a) Experiment. Calculated from: b) Eq. (3); c) Eq. (4); d) Eq. (5).
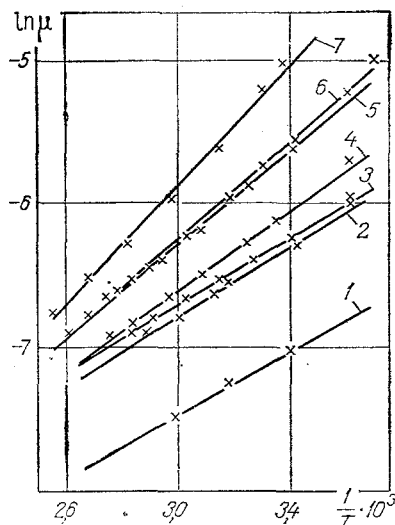
Fig. 3. Temperature dependence of viscosity μ (N· sec/m²) of electrolyte (1 M LiClO₄) based on aprotic solvents and mixtures of them: 1) THF; 2) γ-BL:THF (1:1); 3) PC:THF (1:1); 4) γ-BL:THF (7:3); 5) PC:THF (7:3); 6) γ-BL; 7) PC; the points are our experimental data.

the variable component the difference between the values in question increases, tending at the limit to the values for the one-component solvent (PC or γ-BL).

Turning now to a consideration of the viscosity of electrolytes (1 M LiClO₄) based on these solvents we notice first of all the appreciable (though unequal) increase in the viscosity of the electrolytes in comparison with the pure solvents (compare Figs. 3 and 1). For instance, the viscosity of a PC electrolyte at 273°K is 2.78 times greater than the viscosity of the pure solvent, whereas for a THF electrolyte it is only 1.9 times greater; the difference in the change (increase) in activation energy of the viscosity is appreciably smaller: by a factor of 1.35 and 1.25, respectively. This difference decreases a little with increase in temperature. The observed increase in viscosity can be attributed to the solvation of lithium ions [1].

The viscosity of electrolytes based on a two-component solvent mixture behaved in the same way as in mixtures of pure solvents (Fig. 4).

Figures 2 and 4 show plots of the viscosity of solvent mixtures and electrolytes based on them against the composition (molar or volume) of the mixture, calculated from the empirical equations [7] of:

Zdanovskii

$$\mu_{mix} = (\bar{x}_1 d_1 + \bar{x}_2 d_2)/(\bar{x}_1 d_1/\mu_1 + \bar{x}_2 d_2/\mu_2), \tag{3}$$

where x_1 and x_2 are the volume fractions, d_1 and d_2 are the densities, and μ_1 and μ_2 are the viscosities, of the mixture components;

Arrhenius

$$\ln \mu_{mix} = x_1 \ln \mu_1 + x_2 \ln \mu_2; \tag{4}$$

Kendall and Monroe
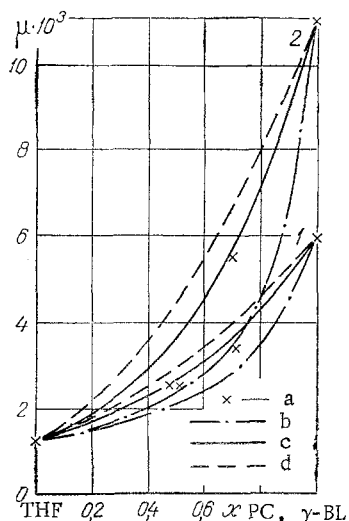
$$\mu_{mix}^{1/3} = x_1 \mu_1^{1/3} + x_2 \mu_2^{1/3}; \tag{5}$$

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Fig. 4. Plots of viscosity μ ($N \cdot sec/m^2$) of electrolyte (1 M LiClO$_4$) based on a solvent mixture against mole (volume) fraction (x, $\bar{x}$) of variable component ($T = 273°K$): 1) γ-BL:THF; 2) PC:THF; a) Experiment; calculation from: b) (3); c) (4); d) (5).

in (4) and (5) x_1 and x_2 are mole fractions of the mixture components.

A comparison with experimental data shows that the best equation for calculating the viscosity of two-component solvent mixtures is Zdanovskii's Eq. (3). For calculation of the viscosity of electrolytes there is no single equation that is best: For an electrolyte based on a γ-BL:THF mixture the best agreement between calculation and experiment is obtained when the Arrhenius Eq. (4) is used; for an electrolyte based on a PC:THF mixture with a PC mole fraction less than five the best equation is Zdanovskii's, and for mixtures with mole fractions greater than 0.5 the Arrhenius equation is best. These results can be attributed to the complex composition of the electrolyte and the interaction between its components.

NOTATION

μ, viscosity, $N \cdot sec/m^2$; E_μ, viscosity activation energy, kJ/mole; T, temperature, $°K$; d, density, kg/m^3; x, mole fraction of component in mixture; $\bar{x}$, volume fraction of component in mixture.

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