NOTATION

T, temperature, °K; p, pressure, N/m^2; M_i, molecular weight of the i-th component of the mixture, kg/kmole; X_i, molar fraction of the i-th component of the mixture (the subscript 1 refers to the light component); λ_i, thermal conductivity of the i-th component of the mixture, W/(m·°K); D_{ii}, D_{ij}, self-diffusion factor of the i-th component of the mixture and mutual diffusion factor, m^2/sec; ε, σ, parameters of the intramolecular interaction potential functions, °K, Å; $\Omega^{(l,s)*}(T^*)$, collision integrals; A*, B*, quantities expressing the collision integrals.

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RELATIONSHIPS BETWEEN COMPLEXES OF THERMOPHYSICAL PROPERTIES AND COMPRESSIBILITIES OF FLUIDS

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UDC 536.2.022

Based on experimental data for water and toluene, relationships between complexes of thermophysical quantities at a given temperature and pressure and between them and compressibility complexes are established.

It was established [1-11] that the thermal conductivity, dynamic viscosity, thermal activity, isobaric heat capacity, sound velocity, and Prandtl number for fluids are expressed by equations similar to an equation of state resembling the equation of state for actual gases in virial form which include a combination of only two of the so-called virial coefficients depending on the type of fluid and the temperature. These equations for water and six aromatic hydrocarbons (benzene, toluene, ethylbenzene, m-, p-, and o-xylols) have the following form:

for water

$$\frac{pv}{RT} = 1 + B\rho + E\rho^4, \tag{1}$$

$$\frac{\lambda}{\lambda_s'} = 1 + B_\lambda\rho + E_\lambda\rho^4, \tag{2}$$

$$\frac{\eta}{\eta_s'} = 1 + B_\eta\rho + E_\eta\rho^4, \tag{3}$$

M. Azizbekov Azerbaidzhan Institute of Petroleum and Chemistry, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 33, No. 1, pp. 91-96, July, 1977. Original article submitted June 22, 1976.

$$\frac{c_p}{c'_{p_s}} = 1 + B_{c_p}\rho + E_{c_p}\rho^4, \tag{4}$$

$$\frac{u}{u'_s} = 1 + B_u\rho + E_u\rho^4, \tag{5}$$

$$\frac{\mathrm{Pr}}{\mathrm{Pr}'_s} = 1 + B_{\mathrm{Pr}}\rho + E_{\mathrm{Pr}}\rho^4, \tag{6}$$

$$\frac{\varkappa}{\varkappa'_s} = 1 + B_\varkappa\rho + E_\varkappa\rho^4; \tag{7}$$

for aromatic hydrocarbons

$$\frac{pv}{RT} = 1 + B\rho + H\rho^7, \tag{1'}$$

$$\frac{\lambda}{\lambda'_s} = 1 + B_\lambda\rho + H_\lambda\rho^7, \tag{2'}$$

$$\frac{\eta}{\eta'_s} = 1 + B_\eta\rho + H_\eta\rho^7, \tag{3''}$$

$$\frac{c_p}{c'_{p_s}} = 1 + B_{c_p}\rho + H_{c_p}\rho^7, \tag{4'}$$

$$\frac{u}{u'_s} = 1 + B_u\rho + H_u\rho^7, \tag{5'}$$

$$\frac{\mathrm{Pr}}{\mathrm{Pr}'_s} = 1 + B_{\mathrm{Pr}}\rho + H_{\mathrm{Pr}}\rho^7, \tag{6'}$$

$$\frac{\varkappa}{\varkappa'_s} = 1 + B_\varkappa\rho + H_\varkappa\rho^7. \tag{7'}$$

For $pv = Rt$, $\lambda = \lambda'_s$, $\eta = \eta'_s$, $c_p = c'_{p_s}$, $u = u'_{p_s}$, $\mathrm{Pr} = \mathrm{Pr}'_s$, and $\varkappa = \varkappa'_s$, Eqs. (1)-(7) and (1')-(7') are transformed into the following expressions:

for water

$$\frac{\dfrac{\lambda}{\lambda'_s} - 1}{E_\lambda\rho} - \frac{\dfrac{pv}{RT} - 1}{E\rho} = \rho_0^3 - \rho_s^3, \tag{8}$$

$$\frac{\dfrac{\eta}{\eta'_s} - 1}{E_\eta\rho} - \frac{\dfrac{pv}{RT} - 1}{E\rho} = \rho_0^3 - \rho_s^3, \tag{9}$$

$$\frac{\dfrac{c_p}{c'_{p_s}} - 1}{E_{c_p}\rho} - \frac{\dfrac{pv}{RT} - 1}{E\rho} = \rho_0^3 - \rho_s^3, \tag{10}$$

$$\frac{\dfrac{u}{u'_s} - 1}{E_u\rho} - \frac{\dfrac{pv}{RT} - 1}{E\rho} = \rho_0^3 - \rho_s^3, \tag{11}$$

$$\frac{\dfrac{\mathrm{Pr}}{\mathrm{Pr}'_s} - 1}{E_{\mathrm{Pr}}\rho} - \frac{\dfrac{pv}{RT} - 1}{E\rho} = \rho_0^3 - \rho_s^3, \tag{12}$$

$$\frac{\dfrac{\varkappa}{\varkappa'_s}-1}{E_\varkappa\rho}-\frac{\dfrac{pv}{RT}-1}{E\rho}=\rho_0^3-\rho_s^3; \tag{13}$$

for aromatic hydrocarbons

$$\frac{\dfrac{\lambda}{\lambda'_s}-1}{H_\lambda\rho}-\frac{\dfrac{pv}{RT}-1}{H\rho}=\rho_0^6-\rho_s^6, \tag{8'}$$

$$\frac{\dfrac{\eta}{\eta'_s}-1}{H_\eta\rho}-\frac{\dfrac{pv}{RT}-1}{H\rho}=\rho_0^6-\rho_s^6, \tag{9'}$$

$$\frac{\dfrac{c_p}{c'_{p_s}}-1}{H_{c_p}\rho}-\frac{\dfrac{pv}{RT}-1}{H\rho}=\rho_0^6-\rho_s^6, \tag{10'}$$

$$\frac{\dfrac{u}{u'_s}-1}{H_u\rho}-\frac{\dfrac{pv}{RT}-1}{H\rho}=\rho_0^6-\rho_s^6, \tag{11'}$$

$$\frac{\dfrac{\mathrm{Pr}}{\mathrm{Pr}'_s}-1}{H_{\mathrm{Pr}}\rho}-\frac{\dfrac{pv}{RT}-1}{H\rho}=\rho_0^6-\rho_s^6, \tag{12'}$$

$$\frac{\dfrac{\varkappa}{\varkappa'_s}-1}{H_\varkappa\rho}-\frac{\dfrac{pv}{RT}-1}{H\rho}=\rho_0^6-\rho_s^6. \tag{13'}$$

In Eqs. (8)-(13) and (8')-(13'):

for water

$$-\frac{B}{E}=\rho_0^3, \tag{14}$$

$$-\frac{B_\lambda}{E_\lambda}=-\frac{B_\eta}{E_\eta}=-\frac{B_{c_p}}{E_{c_p}}=-\frac{B_u}{E_u}=-\frac{B_{\mathrm{Pr}}}{E_{\mathrm{Pr}}}=-\frac{B_\varkappa}{E_\varkappa}=\rho_s^3, \tag{15}$$

for aromatic hydrocarbons

$$-\frac{B}{H}=\rho_0^6, \tag{14'}$$

$$-\frac{B_\lambda}{H_\lambda}=-\frac{B_\eta}{H_\eta}=-\frac{B_{c_p}}{H_{c_p}}=-\frac{B_u}{H_u}=-\frac{B_{\mathrm{Pr}}}{H_{\mathrm{Pr}}}=-\frac{B_\varkappa}{H_\varkappa}=\rho_s^6. \tag{15'}$$

Thus, according to Eqs. (8)-(13) and (8')-(13'), a relationship between the six enumerated complexes of thermophysical quantities and the compressibility complex is established. From the specified equations it first follows that at a given temperature and pressure the following equalities must hold between the enumerated complexes of thermophysical quantities:

for water

$$\frac{\frac{\lambda}{\lambda_s'}-1}{E_\lambda\rho}=\frac{\frac{\eta}{\eta_s'}-1}{E_\eta\rho}=\frac{\frac{c_p}{c_{p_s}'}-1}{E_{c_p}\rho}=\frac{\frac{u}{u_s'}-1}{E_u\rho}=\frac{\frac{\mathrm{Pr}}{\mathrm{Pr}_s'}-1}{E_{\mathrm{Pr}}\rho}=\frac{\frac{\varkappa}{\varkappa_s'}-1}{E_\varkappa\rho}, \tag{16}$$

for aromatic hydrocarbons

$$\frac{\frac{\lambda}{\lambda_s'}-1}{H_\lambda\rho}=\frac{\frac{\eta}{\eta_s'}-1}{H_\eta\rho}=\frac{\frac{c_p}{c_{p_s}'}-1}{H_{c_p}\rho}=\frac{\frac{u}{u_s'}-1}{H_u\rho}=\frac{\frac{\mathrm{Pr}}{\mathrm{Pr}_s'}-1}{H_{\mathrm{Pr}}\rho}=\frac{\frac{\varkappa}{\varkappa_s'}-1}{H_\varkappa\rho}, \tag{16'}$$

and, second, since the right sides of Eqs. (8)-(13) and (8')-(13') are functions of temperature alone, it follows that the differences between specified compressibility complexes (independently of pressure) and between the specified complexes and the compressibility complex (independently of pressure) are constant for a given temperature and a given fluid.

The first conclusion was confirmed [1] in the case of toluene for two complexes — thermal conductivity and viscosity — at 50°C and 300 bar. A typical calculation for all six bar was carried out for the following values of the coefficients in Eqs. (1)-(7): $B = 5.6116$; $E = 5.1976$; $B_\lambda = -0.7306$; $E_\lambda = 0.8302$; $B_\eta = -0.5442$; $E_\eta = 0.6184$; $B_{cr} = 0.3081$; $E_{cr} = -0.3501$; $B_u = 1.3236$; $E_u = 1.5039$; $B_{Pr} = 0.5792$; $E_{Pr} = -0.6582$; $B_\varkappa = -0.3319$; $E_\varkappa$ 0.3772. The results are presented in Table 1 and they indicate that complexes for viscosity and Prandtl number at 100°C and 100 bar constitute exceptions. A check showed that if the values of the viscosity* and Prandtl number† in these parameters were increased by 0.14 and 0.23%, which fell within the limits of experimental error, this led to smoothing of the deviation.

The second conclusion is illustrated rather well by the data in Table 2, which were obtained from calculations based on Eq. (8) for water at 100°C and pressures of 100 and 500 bar.

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*$\eta = 2810 \cdot 10^{-7}$ was replaced by the value $2814 \cdot 10^{-7}$.

†$\mathrm{Pr} = 1.71$ was replaced by the value 1.714.

TABLE 1. Values of Six Complexes of Thermophysical Quantities for Water at t = 100°C

p, bar	$\frac{\frac{\lambda}{\lambda_s'}-1}{E_\lambda\rho}$	$\frac{\frac{\eta}{\eta_s'}-1}{E_\eta\rho}$	$\frac{\frac{c_p}{c_{p_s}'}-1}{E_{cp}\rho}$	$\frac{\frac{u}{u_s'}-1}{E_u\rho}$	$\frac{\frac{\mathrm{Pr}}{P_{r_s}'}-1}{E_{\mathrm{Pr}}\rho}$	$\frac{\frac{\varkappa}{\varkappa_s'}-1}{E_\varkappa\rho}$
100	0,0147	0,0120	0,0154	0,0142	0,0183	0,0154
500	0,0596	0,0590	0,0685	0,0620	0,0538	0,0635

TABLE 2. Difference between Complexes of Thermal Conductivity and Compressibility for Water* at t = 100°C from Eq. (8)

p, bar	$\frac{\frac{\lambda}{\lambda_s'}-1}{E_\lambda\rho}$	$\frac{\frac{pv}{RT}-1}{E\rho}$	$\rho_0^3-\rho_s^3$
100	0,0147	—0,1878	0,20
500	0,0596	—0,1381	0,20

*$R = 4.615$ bar·cm^3/(g·deg)

In conclusion, it must be pointed out that the relations we have established are of practical importance, since they make it possible to calculate complexes of the six cited thermophysical properties by means of a more precisely determined complex — compressibility — and thereby they first match the thermophysical quantities among themselves and, second, they provide an opportunity for validly extrapolating the equations given to high pressures as was demonstrated in [2, 5].

NOTATION

p, pressure; v, specific volume; ρ, density; ρ_s, density of saturated fluid; ρ_0, density of fluid at $pv = RT$; T, absolute temperature; R, gas constant; λ, coefficient of thermal conductivity; η, coefficient of dynamic viscosity; c_p, isobaric heat capacity; u, sound velocity; Pr, Prandtl number; $\varkappa$, coefficient of thermal activity; λ'_s, η'_s, c'_{p_s}, u'_s, Pr'_s, $\varkappa'_s$, corresponding parameters for saturated fluid; B, E, H; B_λ, E_λ, H_λ; B_η, E_η, H_η; B_{c_p}, E_{c_p}, H_{c_p}; B_u, E_u, H_u; B_{Pr}, E_{Pr}, H_{pr}, $B_\varkappa$, $E_\varkappa$, $H_\varkappa$, coefficients depending only on temperature; $[(pv/RT)-1]/E\rho$, $[(pv/RT)-1]/H\rho$, compressibility complexes; $[(\lambda/\lambda'_s)-1]/E_\lambda\rho$, $[(\lambda/\lambda'_s)-1]/H_\lambda\rho$, thermal-conductivity complexes; $[(\eta/\eta'_s)-1]/E_\eta\rho$, $[(\eta/\eta'_s)-1]/H_\eta\rho$, viscosity complexes; $[(c_p/c'_{p_s})-1]/E_{c_p}\rho$, $[(c_p/c'_{p_s})-1]/H_{c_p}\rho$, heat-capacity complexes; $[(u/u'_s)-1]/E_u\rho$, $[(u/u'_s)-1]/H_u\rho$, sound-velocity complexes; $[(\mathrm{Pr}/\mathrm{Pr}'_s)-1]/E_{\mathrm{Pr}}\rho$, $[(\mathrm{Pr}/\mathrm{Pr}'_s)-1]/H_{\mathrm{Pr}}\rho$, Prandtl-number complexes; $[(\varkappa/\varkappa'_s)-1]/E_\varkappa\rho$, $[(\varkappa/\varkappa'_s)-1]/H_\varkappa\rho$, thermal-activity complexes. The first complexes are those for water and the second, those for aromatic hydrocarbons.

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