Keyword　新規冷媒　蒸気圧　地球温暖化　冷凍空調

新規冷媒の蒸気圧測定と汎用状態方程式による相関

Vapor pressure measurement for new refrigerants and correlation by generalized equations of state

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研究背景

Background The substance trans-1,2-dichloroethene [R1130(E)] is a possible refrigerant with a low global-warming potential (GWP) and negligible ozone-depletion potential (ODP) for centrifugal chillers, high-temperature heat pumps, and organic Rankin cycles. However, available experimental vapor pressure data of R1130(E) are generally scattered and inconsistent, and an equation of state has still not been established for this fluid. Additional vapor pressure data are required to develop an accurate and wide-ranging equation of state.

研究目的

Objective This work presents new measurements of the vapor pressure of R1130(E), obtained using a proven experimental apparatus that has been successfully employed in our previous studies. The data obtained in this work are verified using a correlation based on the corresponding states principle. Comparisons with several representative experimental data are made to identify those that are consistent with the present measurements and correlation, which will be used to develop a Helmholtz energy equation of state.

研究概要

Experimental Setup The experimental setup used in this work is shown in Fig. 2. The sample fluid is filled into a pressure vessel, and the mass of the fluid transferred into the vessel is measured using a precision balance with an uncertainty of 1 mg. The inner volume of the vessel including the tubing is calibrated in advance as a function of temperature and pressure. The pressure vessel is placed in a thermostatic silicone oil bath. A pressure sensor is installed near the inlet of the vessel for direct pressure measurement. The temperature in the bath is measured by a 25 Ω standard platinum resistance thermometer with an uncertainty of 1 mK, mounted close to the vessel. The thermometer is calibrated against the ITS-90 standard using an AC thermometer bridge. A PID controller monitors the temperature and continuously adjusts the electric power load of the sub-heaters.

Results and Discussion A total of 21 vapor pressure data were obtained in the temperature range from 300 K to 400 K, which are given in Table 1 and Fig. 3. The data are successfully correlated with the Wagner-type correlation. Figure 4 shows relative deviations and absolute differences in the present data from values calculated with the correlation, along with those in the representative data. The average deviation and difference between the present data and the correlation are 0.020 % and 0.034 kPa, with a maximum difference of 0.095 kPa, which is sufficiently smaller than the expanded experimental uncertainty in the pressure measurement.

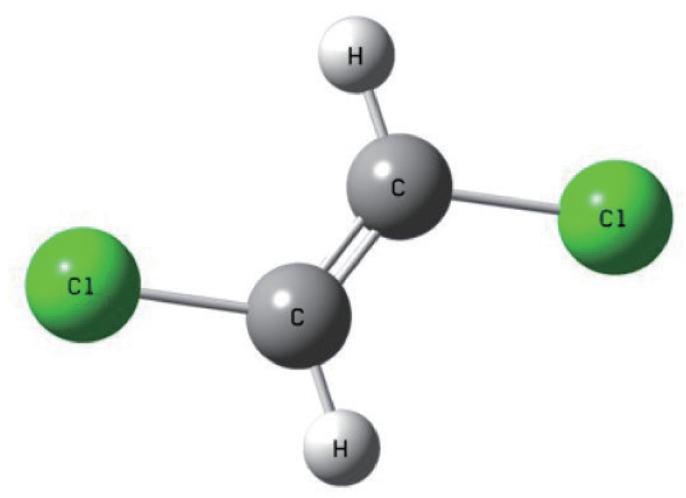

Fig. 1: Molecular structure of R1130(E) obtained from the geometry optimization with Gaussian 09 (Calculation method: RB3LYP, Basic set: CC-pVDZ)

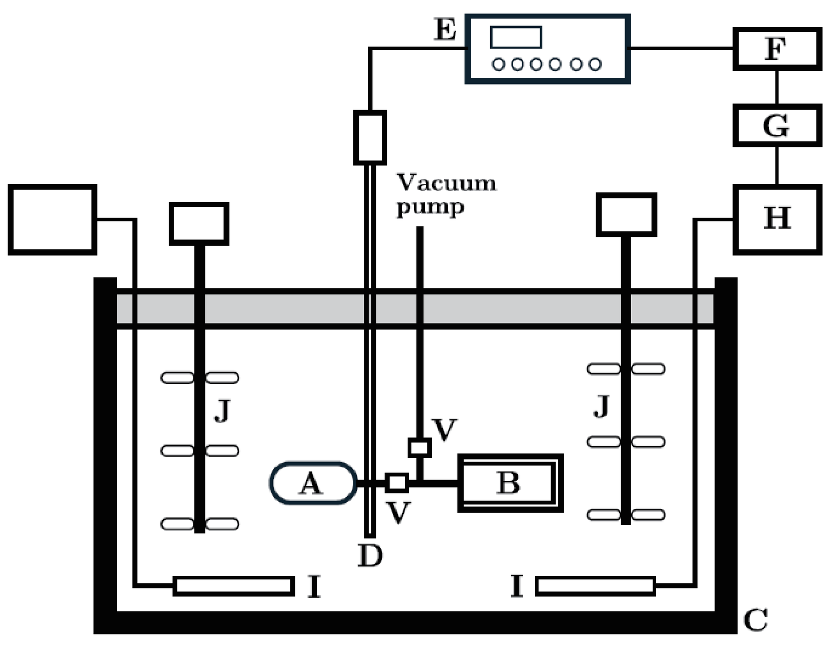

Fig. 2: Experimental setup for the vapor pressure measurement. A: pressure vessel, B: pressure transducer, C: thermostatic silicone-oil bath, D: 25 Ω standard PRT, E: thermometer bridge, F: DMM, G: PID temperature controller, H: power supply, I: heater, J: stirrer, V: valve.

Table 1: Vapor pressures of R1130(E) obtained in this work. The combined expanded uncertainties U (k = 2) are U(T) = 5 mK and U(ps) = 1 kPa.

T/K	p_s/MPa	T/K	p_s/MPa
300.000	0.0481	355.000	0.2875
305.000	0.0584	360.000	0.3280
310.000	0.0703	365.000	0.3727
315.000	0.0841	370.000	0.4219
320.000	0.1000	375.000	0.4759
325.000	0.1182	380.000	0.5348
330.000	0.1390	385.000	0.5991
335.000	0.1624	390.000	0.6690
340.000	0.1887	395.000	0.7448
345.000	0.2181	400.000	0.8268
350.000	0.2510		

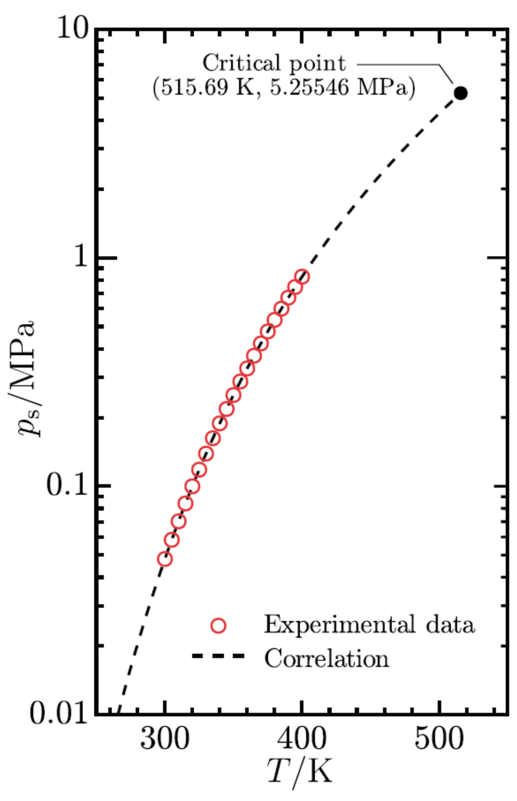

Fig. 3: Present vapor pressures and correlation plotted on a ps-T diagram

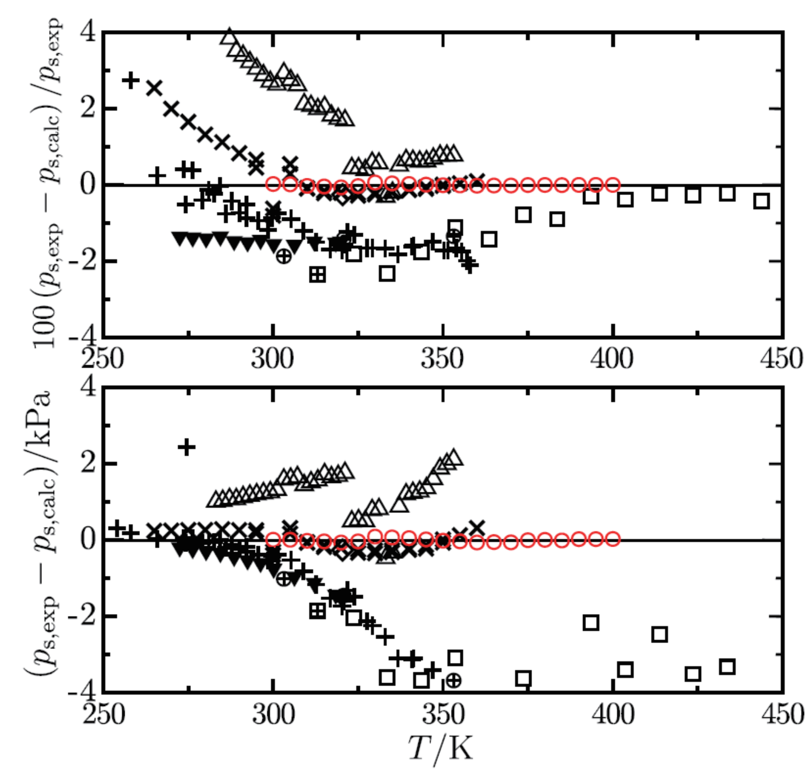

Fig. 4: Relative deviations (top panel) and absolute differences (bottom panel) in representative experimental vapor pressures from values calculated with the correlation. (+) Ketelaar et al. [1], (▼) Machát and Boublík [2]; (◇) Kovac et al. [3], (⊞) Mato and Berro [4], (◎) Hiaki et al. [5], (⊕) Giles and Wilson [6], (□) Tanaka et al. [7]; (△) Lombardo et al. [8]; (×) Rowane and Outcalt [9]; (○) Present data.

総括

Conclusions New experimental vapor pressure data for R1130(E) were obtained at temperatures from 300 K to 400 K. Comparisons with representative experimental datasets clarified which data are consistent with the present vapor pressure measurements; this suggests suitable datasets that will contribute to developing a Helmholtz energy equation of state for this fluid.

References
1. J. Ketelaar, P.V. Velden, P. Zalm, Recl. Trav. Chim. Pays-Bas. 66, 721 (1947).
2. V. Machát, T. Boublík, J. Chem. Thermodyn. 17(9), 887 (1985).
3. A. Kovac, J. Svoboda, I. Ondrus, Chem. Zvesti 39, 729 (1985).
4. F.A. Mato, C. Berro, J. Chem. Eng. Data 36(3), 262 (1991).
5. T. Hiaki, M. Nanao, S. Urata, J. Murata, Fluid Phase Equilib. 194, 969 (2002).
6. N.F. Giles, G.M. Wilson, J. Chem. Eng. Data 51(6), 1973 (2006).
7. K. Tanaka, C. Kondou, S. Fukuda, R. Akasaka, Int. J. Thermophys. 43(5), 69 (2022).
8. G. Lombardo, D. Menegazzo, L. Fedele, S. Bobbo, M. Scattolini, in International Congresso of Refrigeration (Paris, France) (2023).
9. A.J. Rowane, S.L. Outcalt, Int. J. Thermophys. 45(7), 96 (2024).

指導教員コメント

蒸気圧は冷媒として最も重要な熱物性値の一つである．本研究では，次世代冷媒として期待されている R1130(E)の蒸気圧を高精度に測定し，対応状態原理に基づいた相関式を作成した．これまでに発表されている蒸気圧データは熱力学的一貫性に欠けており，高精度な状態方程式を開発するための障壁となっていた．本研究で得られたデータによって一貫性のある蒸気圧のデータセットを確立することが可能になり，今後の状態方程式開発における重要な知見となった．本研究成果をまとめた論文は International Journal of Thermophysics 誌に掲載されることが決定している．

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