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THERMODYNAMIC PROPERTIES OF METHYL ACETATE-BENZENE AND METHYL ACETATE-CYCLOHEXANE MIXTURES*

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Excess Gibbs free energies were determined for methyl acetate-benzene system at 30°, 40°, and 50°C and for methyl acetate-cyclohexane system at 35° and 40°C. Excess enthalpy of mixing data were obtained for methyl acetate-benzene system at 25° and 35°C and for methyl acetate-cyclohexane system at 25°, 35°, and 45°C. All experimental data for each system were simultaneously well correlated with the NRTL equation, whose parameters were assumed to be expressed by a linear function of temperature.

Introduction

Isobaric vapor-liquid equilibrium data for many binary systems frequently deviate from the so-called area condition which is strictly applicable to isothermal conditions, because the heat of mixing term in the Gibbs-Duhem equation under isobaric conditions is usually not negligible. Available heat of mixing data are fewer than vapor-liquid equilibrium data for nonideal

solutions. Although the temperature dependence of activity coefficients is theoretically in close relation with heat of mixing data, heat of mixing data estimated from the activity coefficients are not accurate. From a theoretical and practical standpoint, it is desirable to combine the excess Gibbs free energy data with excess heat of mixing data in a single equation.

In this work the isothermal vapor-liquid equilibrium data for the methyl acetate-benzene system at 30°, 40° and 50°C and for the methyl acetate-cyclohexane system at 35° and 40°C are measured, and excess enthalpy data are obtained for the methyl acetate-benzene system at 25° and 35°C and for the methyl acetate-cyclohexane system at 25°, 35° and 45°C. These data are used to check the accuracy of equilibri-

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Table 1 Physical constants of compounds

Compound	Bp. [°C]	Density at 25°C	Refractive index at 25°C n_D^{25}
Benzene	80.1	0.8735	1.4979
	80.1(13)	0.87364(13)	1.49792(13)
Cyclohexane	80.8	0.7739	1.4236
	80.72(13)	0.7737(13)	1.42354(15)
Methyl acetate	56.8	0.9273	1.3588
	56.9(13)	0.9279(13)	1.3587(7)

um data for the two systems previously observed by Nagata^{5,6} at 760 mmHg.

Experimental

Cyclohexane of guaranteed grade was used without further purification. Chemically pure benzene was purified by recrystallization several times. Methyl acetate was purified in accordance with Hurd's procedure¹⁵. Experimental apparatus used to obtain isothermal vapor-liquid equilibrium data and excess enthalpies of mixing were the same as those described in the previous papers^{2,10,11}. **Table 1** lists the physical constants of materials used in this work.

Data Reduction

Experimental equilibrium data were analyzed by a conventional method. First, the coexistence equation was used to calculate the equilibrium vapor mole fractions from the total pressure-liquid mole fraction data. The equation is expressed by

$$\frac{dy_1}{dP} = \frac{\psi - (1 - 2y_1)(y_1 - x_1)(\delta_{12}/RT)}{\frac{(y_1 - x_1)}{y_1(1 - y_1)} - (y_1 - x_1)(2P\delta_{12}/RT)} \quad (1)$$

$$\psi = \frac{y_1(1 - y_1)\delta_{12} - v^L + x_1B_{11} + x_2B_{22}}{RT} + \frac{1}{P} \quad (2)$$

This equation is derived from the Gibbs-Duhem equation and is valid under isothermal conditions and at low pressures. The derivation of the equation is described in detail in Van Ness's monograph¹⁴. Second virial coefficients were calculated using the correlation of O'Connell and Prausnitz⁴. The critical constants, liquid molar volumes, and the constants of the Antoine equation and a six-constant vapor pressure equation were obtained from the literature^{7,12,16}. The liquid molar volume of a mixture was assumed to be a linear function of mole fraction between the values of molar volume for the pure components. This means negligible volume change on mixing. In addition, the pressure effect on molar volume was neglected. The total pressure data vs. liquid composition was fitted with the Forsythe polynomials⁹. The Runge-Kutta-Gill numerical integration method was used to perform the integration of Eq.(1) in a stepwise manner. All inte-

grations started at the pure component compositions. Secondly, a simultaneous fit of experimental vapor-liquid equilibrium and excess enthalpy of mixing data was attempted using the nonrandom two-liquid (NRTL) equation. The NRTL equation gives the following expressions for the excess Gibbs free energy, g^E , and the activity coefficients, γ 's.

$$\frac{g^E}{RT} = x_1x_2 \left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}} \right] \quad (3)$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2G_{21}} \right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2} \right] \quad (4)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1G_{12}} \right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2} \right] \quad (5)$$

where

$$\tau_{12} = (g_{12} - g_{22})/RT; \quad \tau_{21} = (g_{21} - g_{11})/RT;$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}); \quad \text{and} \quad G_{21} = \exp(-\alpha_{21}\tau_{21}).$$

The parameters of the NRTL equation are assumed to be a linear function of temperature as proposed by Asselineau and Renon¹.

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15) \quad (6)$$

$$g_{12} - g_{22} = C_2 + D_2(T - 273.15) \quad (7)$$

$$\alpha_{12} = C_3 + D_3(T - 273.15) \quad (8)$$

The heats of mixing, h^E , are calculated from the excess Gibbs free energy data through the Gibbs-Helmholtz relation.

$$\frac{h^E}{R} = \left[\frac{\partial(g^E/RT)}{\partial(1/T)} \right]_{P,x} \quad (9)$$

$$\begin{aligned} h^E = & \frac{x_1x_2 \exp(-\alpha_{12}\tau_{21})}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} \\ & \times \left[\left(1 - \frac{\alpha_{12}\tau_{21}x_1}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} \right) \right. \\ & \times (C_1 - 273.15D_1) + \frac{\tau_{21}^2x_1D_3RT^2}{x_1 + x_2 \exp(-\alpha_{12}\tau_{21})} \\ & + \frac{x_1x_2 \exp(-\alpha_{12}\tau_{12})}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})} \\ & \times \left[\left(1 - \frac{\alpha_{12}\tau_{12}x_2}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})} \right) \right. \\ & \times (C_2 - 273.15D_2) + \frac{\tau_{12}^2x_2D_3RT^2}{x_2 + x_1 \exp(-\alpha_{12}\tau_{12})} \left. \right] \end{aligned} \quad (10)$$

The following objective function was minimized to obtain the constants C 's and D 's as suggested by Asselineau and Renon¹.

$$\begin{aligned} Q = & \sum \{100(y_{\text{exptl}} - y_{\text{calc}})\}^2 \\ & + \sum \left\{ 100 \frac{(P_{\text{exptl}} - P_{\text{calc}})}{P_{\text{exptl}}} \right\}^2 \\ & + \sum \left\{ \frac{h_{\text{exptl}}^E - h_{\text{calc}}^E}{5} \right\}^2 \end{aligned} \quad (11)$$

Results

The agreement between smoothed experimental vapor mole fractions and calculated values obtained from the coexistence equation is good. This may suggest that the experimental data are thermodynamically consistent. How correctly the NRTL equation does a simul-

Table 2 Experimental isothermal vapor-liquid equilibrium data for binary systems

x_1	y_1	P [mmHg]	γ_1	γ_2	ϕ_1	ϕ_2	g^E [cal/mol]	Δy^a		$100\Delta P_{rel}^b$	
								I	II	I	II
Methyl acetate(1)-Benzene(2) at 30 °C											
0.056	0.153	132.4	1.355	0.995	0.992	0.990	7.09	0.001	0.001	-0.49	-0.55
0.065	0.176	134.6	1.365	0.993	0.991	0.990	8.14	0.003	0.003	-0.42	-0.49
0.118	0.271	145.8	1.252	1.008	0.990	0.989	20.19	-0.010	-0.010	-0.95	-1.02
0.168	0.354	157.5	1.239	1.022	0.988	0.989	32.71	-0.011	-0.011	-0.21	-0.26
0.212	0.419	166.4	1.226	1.025	0.987	0.988	37.86	-0.008	-0.008	-0.17	-0.18
0.258	0.474	175.6	1.202	1.040	0.986	0.988	45.97	-0.010	-0.009	0.10	0.11
0.291	0.508	179.9	1.169	1.043	0.986	0.988	45.21	-0.012	-0.012	-0.84	-0.80
0.376	0.590	193.0	1.126	1.059	0.984	0.988	48.24	-0.011	-0.010	-1.43	-1.34
0.417	0.619	200.5	1.105	1.094	0.983	0.987	56.57	-0.016	-0.015	-0.85	-0.73
0.524	0.708	216.5	1.084	1.108	0.981	0.987	55.01	-0.005	-0.004	-0.53	-0.38
0.619	0.768	227.9	1.047	1.158	0.980	0.987	50.68	-0.005	-0.004	-0.92	-0.75
0.761	0.855	246.0	1.021	1.246	0.978	0.988	41.15	-0.001	-0.001	-0.21	-0.08
0.778	0.864	246.2	1.010	1.259	0.978	0.988	35.44	-0.001	-0.001	-0.88	-0.75
0.839	0.903	252.0	1.001	1.268	0.978	0.988	23.62	0.003	0.002	-1.12	-1.01
0.868	0.920	258.0	1.009	1.306	0.977	0.988	25.81	0.003	0.002	0.09	0.18
0.915	0.950	260.3	0.997	1.279	0.977	0.989	10.82	0.005	0.004	-0.82	-0.76
Methyl acetate(1)-Benzene(2) at 40 °C											
0.081	0.203	212.0	1.328	1.004	0.988	0.986	16.54	0.002	0.001	0.44	0.37
0.136	0.305	230.8	1.291	1.013	0.986	0.985	28.42	0.000	0.000	0.86	0.80
0.236	0.443	257.5	1.202	1.023	0.983	0.984	37.79	-0.006	-0.006	-0.33	-0.34
0.421	0.630	305.3	1.130	1.062	0.978	0.983	53.63	-0.002	-0.001	0.17	0.28
0.521	0.708	328.9	1.103	1.091	0.976	0.983	57.67	0.002	0.003	0.82	0.97
0.641	0.789	354.5	1.074	1.133	0.973	0.983	56.50	0.006	0.007	1.50	1.66
0.761	0.854	378.1	1.042	1.256	0.971	0.983	53.54	0.000	0.000	2.18	2.32
0.844	0.903	391.3	1.027	1.324	0.970	0.983	41.31	0.001	0.001	2.12	2.22
0.914	0.945	397.7	1.008	1.384	0.969	0.984	22.09	0.001	0.000	1.07	1.13
Methyl acetate(1)-Benzene(2) at 50 °C											
0.080 ^c	0.194	309.8	1.294	1.006	0.984	0.982	16.45	0.000	0.000	-0.32	-0.39
0.191	0.381	364.4	1.245	1.030	0.979	0.979	42.34	-0.001	-0.001	1.17	1.13
0.254 ^c	0.461	387.0	1.200	1.032	0.977	0.979	45.03	-0.002	-0.002	0.37	0.37
0.371 ^c	0.577	432.7	1.145	1.073	0.973	0.977	60.66	-0.006	-0.005	1.01	1.10
0.414 ^c	0.614	445.7	1.124	1.082	0.972	0.977	60.62	-0.006	-0.005	0.67	0.78
0.466 ^c	0.657	464.4	1.111	1.099	0.970	0.977	63.83	-0.004	-0.003	1.11	1.24
0.548 ^c	0.716	483.7	1.070	1.120	0.969	0.977	56.72	-0.004	-0.003	0.02	0.18
0.650	0.784	513.2	1.046	1.166	0.966	0.977	53.27	-0.001	-0.001	0.36	0.53
0.702 ^c	0.816	525.1	1.030	1.194	0.965	0.977	47.33	-0.001	0.000	0.11	0.27
0.759 ^c	0.851	540.0	1.021	1.230	0.964	0.977	41.92	0.000	0.000	0.30	0.45
0.811 ^c	0.884	555.3	1.019	1.255	0.963	0.977	37.42	0.003	0.002	0.87	1.00
0.927 ^c	0.955	581.2	1.006	1.321	0.961	0.978	16.57	0.003	0.003	0.94	1.00
Methyl acetate(1)-Cyclohexane(2) at 35 °C											
0.111	0.455	255.7	3.167	1.033	0.981	0.981	96.19	-0.007	-0.012	-0.13	-1.30
0.231	0.592	312.3	2.404	1.089	0.976	0.978	164.16	0.005	0.006	1.15	0.91
0.440	0.667	349.9	1.587	1.365	0.972	0.977	231.14	-0.010	-0.003	0.40	1.04
0.605	0.712	363.1	1.277	1.736	0.971	0.976	223.99	-0.010	-0.004	0.19	0.98
0.715	0.748	368.8	1.152	2.139	0.970	0.977	194.65	-0.006	-0.002	0.48	1.26
0.753	0.763	369.6	1.118	2.327	0.970	0.977	179.17	-0.004	-0.002	0.50	1.29
0.844	0.817	366.9	1.060	2.828	0.970	0.978	129.50	0.009	0.007	0.16	0.97
0.921	0.878	358.2	1.020	3.641	0.970	0.980	73.61	0.009	0.004	-0.01	0.76
Methyl acetate(1)-Cyclohexane(2) at 40 °C											
0.028	0.201	224.6	4.029	1.004	0.987	0.983	26.42	0.001	-0.007	-0.32	-1.34
0.062	0.334	260.5	3.493	1.003	0.984	0.981	49.97	-0.004	-0.012	-1.65	-2.99
0.174	0.521	347.3	2.567	1.086	0.976	0.976	144.62	-0.012	-0.013	0.21	-0.46
0.322	0.618	399.8	1.885	1.212	0.971	0.974	208.03	-0.012	-0.008	0.24	0.51
0.457	0.670	427.1	1.534	1.395	0.969	0.973	234.10	-0.009	-0.003	0.84	1.50
0.610	0.711	438.2	1.250	1.745	0.967	0.973	219.69	-0.013	-0.007	-0.23	0.56
0.735	0.754	445.1	1.116	2.221	0.967	0.973	181.85	-0.008	-0.006	-0.08	0.71
0.860	0.826	444.2	1.043	2.973	0.966	0.975	117.19	0.004	0.001	0.20	1.01
0.952	0.915	427.3	1.005	4.088	0.967	0.978	44.78	0.005	0.000	0.05	0.68

Calculated vapor pressure data for methyl acetate, 270.4(30°C) 332.4(35°C) 405.5(40°C) 590.4mmHg(50°C)

Calculated vapor pressure data for benzene, 119.3(30°C) 182.8(40°C) 271.3mmHg(50°C)

Calculated vapor pressure data for cyclohexane, 150.6(35°C) 184.7mmHg(40°C)

^a $\Delta y = y_{exptl} - y_{calc}$ ^b $\Delta P_{rel} = (P_{exptl} - P_{calc})/P_{exptl}$ ^c Obtained from ref.(8)

I h^E data and isothermal vapor-liquid equilibrium data only

II h^E data, isothermal vapor-liquid equilibrium data, and isobaric vapor-liquid equilibrium data were included.

taneous fit of experimental vapor-liquid equilibrium data and heat of mixing data is demonstrated in **Tables 2** and **3**, where calculated results I involved only the isothermal vapor-liquid equilibrium data and h^E data, and calculated results II included both the

isothermal and isobaric vapor-liquid equilibrium data previously reported by Nagata^{5,6)} and h^E data. **Table 4** shows these two sets of the NRTL parameters for the two systems and root mean square deviations. The experimental activity coefficients for the two sys-

Fig. 1 Activity coefficient-liquid mole fraction diagram for the methyl acetate (1)-benzene (2) system

tems are compared with the calculated values derived using the parameters (I) listed in Table 4 (Figs. 1 and 2). The liquid-phase activity coefficients were calculated by taking vapor-phase nonideality into account¹²⁾.

$$\gamma_i = \frac{\phi_i y_i P}{\phi_i^s x_i p_i^s \exp \left\{ -\frac{v_i^L (P - p_i^s)}{RT} \right\}} \quad (12)$$

g^E values were calculated from the equation

$$g^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (13)$$

Recently, Hudson and Van Winkle³⁾ reported vapor-liquid equilibrium data for the methyl acetate-benzene system at 1 atm and observed that there is an obvious temperature discrepancy, although the experimental data of Hudson and Van Winkle³⁾ and of Nagata⁵⁾ show relatively good agreement on a y - x diagram. **Table 5** lists the absolute arithmetic mean deviations between isobaric experimental data and calculated results obtained by using the NRTL parameters (I) given in Table 4 for the two systems. The table suggests that the y - x data of Hudson and Van Winkle are better than those of Nagata, but the temperature data of

Table 3 Experimental heat of mixing data for binary systems

Methyl acetate(1)-Benzene(2)

Temp. [°C]	x_1	h^E [cal/mol]	Δh^a [cal/mol]	
			I	II
25.00	0.0537	20.69	1.88	1.79
	0.1188	41.95	3.16	3.01
	0.1510	49.26	1.75	1.57
	0.2197	64.38	0.82	0.60
	0.2634	70.83	-1.11	-1.35
	0.3048	79.79	1.21	0.96
	0.4096	88.15	-1.52	-1.77
	0.4654	91.26	-0.98	-1.22
	0.5104	90.54	-2.07	-2.30
	0.6007	89.42	0.60	0.39
	0.6038	88.70	0.12	-0.08
	0.7118	74.96	-0.87	-1.04
	0.8159	57.67	2.26	2.13
	0.8503	48.61	1.70	1.59
35.00	0.9030	35.14	2.91	2.83
	0.9480	20.12	2.00	1.95
	0.0254	8.56	0.89	0.93
	0.0264	8.93	0.97	1.00
	0.0806	24.89	1.83	1.91
	0.1918	50.96	2.29	2.37
	0.2850	65.60	1.15	1.16
	0.3854	76.16	0.65	0.51
	0.4890	79.74	-0.56	-0.88
	0.5978	77.76	-0.17	-0.66
	0.5983	78.21	0.31	-0.18
	0.6965	68.32	-0.73	-1.31
	0.7969	52.87	-0.42	-1.00
	0.8926	33.97	2.17	1.75
45.00	0.9432	21.36	3.52	3.26
	0.9822	7.16	1.32	1.23
	0.9896	5.07	1.63	1.58
	0.1051	183.37	-1.25	-1.07
	0.1546	249.16	1.37	1.76
	0.2151	307.45	-0.94	-0.37
	0.3104	369.32	-3.65	-3.09
	0.4080	406.35	-0.42	-0.24
	0.5077	413.76	1.14	0.72
	0.6001	392.97	-1.29	-2.21
	0.6929	353.80	1.08	-0.06
	0.7935	277.35	-1.45	-2.35
	0.8556	217.58	1.97	1.43
	0.9054	153.53	0.16	-0.04
35.00	0.0671	126.13	-1.00	-1.11
	0.1654	263.26	1.03	1.33
	0.2178	313.42	-0.68	-0.16
	0.3097	378.88	1.26	1.91
	0.4040	417.82	5.70	6.16
	0.4616	423.31	3.44	3.67
	0.5868	404.20	-0.71	-1.05
	0.7014	354.51	1.13	0.58
	0.8246	252.27	-0.52	-0.73
	0.8897	178.12	1.44	1.55
	0.9462	93.60	-1.08	-0.82
45.00	0.1024	183.04	0.83	0.66
	0.2117	316.05	3.81	4.20
	0.3028	378.16	-1.12	-0.40
	0.5048	423.07	-3.89	-3.41
	0.6000	403.01	-5.13	-4.93
	0.6043	401.81	-4.88	-4.69
	0.7003	362.40	1.97	2.07
	0.7940	290.01	2.48	2.76
	0.8917	178.79	2.02	2.60

Methyl acetate(1)-Cyclohexane(2)

25.00	0.1051	183.37	-1.25	-1.07
	0.1546	249.16	1.37	1.76
	0.2151	307.45	-0.94	-0.37
	0.3104	369.32	-3.65	-3.09
	0.4080	406.35	-0.42	-0.24
	0.5077	413.76	1.14	0.72
	0.6001	392.97	-1.29	-2.21
	0.6929	353.80	1.08	-0.06
	0.7935	277.35	-1.45	-2.35
	0.8556	217.58	1.97	1.43
	0.9054	153.53	0.16	-0.04
35.00	0.0671	126.13	-1.00	-1.11
	0.1654	263.26	1.03	1.33
	0.2178	313.42	-0.68	-0.16
	0.3097	378.88	1.26	1.91
	0.4040	417.82	5.70	6.16
	0.4616	423.31	3.44	3.67
	0.5868	404.20	-0.71	-1.05
	0.7014	354.51	1.13	0.58
	0.8246	252.27	-0.52	-0.73
	0.8897	178.12	1.44	1.55
	0.9462	93.60	-1.08	-0.82
45.00	0.1024	183.04	0.83	0.66
	0.2117	316.05	3.81	4.20
	0.3028	378.16	-1.12	-0.40
	0.5048	423.07	-3.89	-3.41
	0.6000	403.01	-5.13	-4.93
	0.6043	401.81	-4.88	-4.69
	0.7003	362.40	1.97	2.07
	0.7940	290.01	2.48	2.76
	0.8917	178.79	2.02	2.60

^a $\Delta h = h_{\text{exptl}}^E - h_{\text{calc}}^E$

I h^E data and isothermal vapor-liquid equilibrium data only
II h^E data, isothermal vapor-liquid equilibrium data, and isobaric vapor-liquid equilibrium data were included.

Hudson and Van Winkle are exceedingly higher than Nagata's data.

Table 4 Parameters of NRTL equation and root-mean square deviations for binary data

System		C_1 [cal/mol]	C_2 [cal/mol]	C_3	D_1 [cal/mol·°K]	D_2 [cal/mol·°K]	D_3 [1/°K]	Rms deviation		
								$100\Delta y$	$100\Delta P_{rel}$	Δh [cal/mol]
Methyl acetate(1)-benzene(2)	I	-467.26	766.33	0.076244	-11.7506	12.7235	-0.000473	0.6	0.9	1.6
	II	-278.99	551.99	0.091338	-10.6294	11.2593	-0.000687	0.7	0.9	1.6
Methyl acetate(1)-cyclohexane(2)	I	705.93	788.27	0.502770	-3.4730	-1.8450	0.002106	0.8	0.6	2.4
	II	745.08	728.37	0.498266	-3.2301	-2.1525	0.002090	0.7	1.3	2.4

I h^E data and isothermal vapor-liquid equilibrium data only

II h^E data, isothermal vapor-liquid equilibrium data, and isobaric vapor-liquid equilibrium data were included.

Table 5 Calculated results for isobaric data using NRTL parameters obtained from only isothermal vapor-liquid equilibrium data and heat of mixing data

System	Absolute arithmetic mean deviation				
	Press. [mmHg]	$100 \Delta y $	$ \Delta P $ [mmHg]	$ \Delta P_{rel} $ $\times 100$	Ref.
Methyl acetate(1)-benzene(2)	760	1.1	4.5	0.6	(5)
	760	0.3	29.0	3.8	(3)
Methyl acetate(1)-cyclohexane(2)	760	1.2	16.1	2.1	(6)

Conclusions

A simultaneous fit of isothermally observed excess Gibbs free energies and heat of mixing data for the methyl acetate-benzene and methyl acetate-cyclohexane systems is well made with the NRTL equation, whose parameters are assumed to change with temperature linearly over a range of temperature 25° to 50°C. The NRTL equation having the temperature dependent parameters obtained from these data enables us to predict isobaric data at 1 atm accurately.

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Nomenclature

B_{ij}	= second virial coefficient	[ml/mol]
C_1, C_2	= values of $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$ at 0°C	[cal/mol]
C_3	= value of α_{12} at 0°C	
D_1, D_2	= coefficients of temperature change of $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$	[cal/mol·°K]
D_3	= coefficient of temperature change of α_{12}	[°K ⁻¹]
g^E	= excess Gibbs free energy	[cal/mol]
g_{ij}	= energies of interaction between an i - j pair of molecules	[cal/mol]
G_{ij}	= coefficient as defined by $G_{ij}=\exp(-\alpha_{12}\tau_{ij})$	
h^E	= heat of mixing	[cal/mol]
p_i^s	= saturation pressure of pure component i	[atm]
P	= total pressure	[atm]
Q	= objective function as defined by Eq.(11)	
R	= gas constant	[1.987 cal/mol·°K]
T	= absolute temperature	[°K]
v_i^L	= liquid molar volume of pure component i	[ml/mol]
v^L	= liquid molar volume of mixture	[ml/mol]
x_i	= liquid phase mole fraction of component i	
y_i	= vapor phase mole fraction of component i

Fig. 2 Activity coefficient-liquid mole fraction diagram for the methyl acetate (1)-cyclohexane (2) system

<Greek letters>

$\alpha_{12}=\alpha_{21}$ = nonrandomness constant for binary 1-2 interaction

γ_i = activity coefficient of component i

δ_{12} = coefficient as defined by $\delta_{12}=2B_{12}-(B_{11}+B_{22})$ [ml/mol]

τ_{ij} = coefficient as defined by $\tau_{ij}=(g_{ij}-g_{jj})/RT$

ϕ_i^s = fugacity coefficient of pure saturated component i at system temperature and p_i^s

ϕ_i = fugacity coefficient of component i

Ψ = coefficient as defined by Eq.(2)

<Subscript>

i = component

<Superscript>

E = excess

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SOME DEDUCTIONS FROM THE EXTREMUM PRINCIPLES FOR NON-NEWTONIAN FLUIDS*

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A few new inequalities giving estimates for a drag force and so on are obtained. Furthermore, the following proposition is proved theoretically by means of the variational principles in a few special cases: The drag force on a body moving slowly with a constant velocity through a fluid with a given viscosity is smaller than the drag force on the same body moving with the same constant velocity through another fluid with higher viscosity. This proposition yields the conclusion that the Ostwald - de Waele fluid model is not so suitable for use in the analysis of the creeping flow of a polymer solution past a body.

Introduction

It is well known that incompressible, steady-state, creeping flow of a non-Newtonian fluid can be characterized by either of two extremum principles^{4,8)}: one relating to the class of all velocity fields consistent with both the continuity condition and the boundary conditions on velocity, and the other to the class of all stress fields consistent with both the equations of motion without inertial terms and the boundary conditions on stress. The two principles are complementary in the sense that the actual solution minimizes the functional occurring in one, and at the same time maximizes the functional in the other.

Under the situation of no body forces and of no

velocity discontinuity, the minimum of the functional in one is equal to the maximum of the functional in the other. This situation is to be considered here.

For Newtonian or Ostwald-de Waele fluids the common value of these functionals in the actual state is directly connected with that of an important unknown: for example, the drag force exerted on a body moving in a fluid, or the torque of a circular cylinder in a bounded fluid. In such cases an approximate value of the important unknown can be obtained by bracketing it between upper and lower bounds corresponding to arbitrarily-chosen admissible functions in the extremum principles. In this way the error can always be held within any preassigned limits. Moreover, since the first variations of the functionals vanish in the actual state, i.e., since those of the important unknown calculated from the principle of virtual work vanish in the actual state, a close approximation to the actual value of the important unknown can usually be obtained from comparatively simple admissible functions be-

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